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Granulation of Complex Fertilizers Containing Ammonium Sulfate by Melt Technology

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GRANULATION OF COMPLEX FERTILIZERS CONTAINING AMMONIUM SULFATE BY MELT TECHNOLOGY

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GLOSSARY OF ABBREVIATIONS AND SYMBOLS

kilogram	kg	Fahrenheit	F
pound	lb	percent	%
metric	M	phosphorus penoxide	P_2O_5
ton	t	kilogram	k
per	/	square	sq
day	d	centimeter	cm
short ton	st	pounds per square inch	psi
nitrogen	N	hydrogen ion concentration	pH
phosphorus	P	potassium oxide	K_2O
sulfur	S	gram	gm
Tennessee Valley Authority	TVA	weight	wt
degrees	o	millimeter	mm
Centigrade	C	milliliter	ml
		ammonia	NH_3

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SECTION I

INTRODUCTION

PURPOSE AND SCOPE

When the Environmental Protection Agency began to give serious consideration to removal of sulfur dioxide from stack gases by the use of ammonia scrubbing, it was considered essential that suitable processing methods be found which would permit the power companies to sell their by-product ammonium sulfate to the fertilizer industry in order to recover the cost of the ammonia which they used.

During the decade of the 1960's, the advent of granular diammonium phosphate, granular potash, bulk blending marketing stations and the introduction of polyphosphate liquids resulted in the closing of most conventional fertilizer granulation plants. In previous years, most of the by-product ammonium sulfate generated in dispersed chemical and steel plants had been sold to these local granulation plants and reached the market in the form of nitrogen-phosphorus-potash-sulfur (N-P-K-S) mixtures. The shutdown of granulation facilities caused the price of by-product ammonium sulfate to drop to very low levels. The ammonium sulfate market was completely demoralized.

Thus, the purpose of this investigation was to devise a method of modifying the melt granulation process to permit maximum incorporation of ammonium sulfate.

It was considered essential that a new economic process be developed for production of a high nutrient N-P-K-S fertilizer which would be capable of utilizing waste and by-product ammonium sulfate from steel and plastic industries and projected power plant scrubbers. It was most desirable that the new process not be damaging to the environment.

In 1971 and 1972, it seemed to Ferguson Industries that a granulation process in which an ammonium phosphate - polyphosphate melt is produced offered an attractive prospect for the accomplishment of these objectives. Despite the fact that there were no plants in existence in which this was being done, there did not appear to be any inherent reasons for not adopting this melt technology.

If the melt granulation process could be modified to increase the ratio of solid constituents to melt, and to use ammonium sulfate rather than low-melting nitrogenous compounds such as ammonium nitrate or urea, then it would be superior to processes which require the use of aqueous solutions. The melt granulation process would be preferable because its equipment and energy requirements are lower and because its pollution emission is more readily controllable. The use of ammonium nitrate or urea would be incompatible with the objectives of this concept, because they would partially or completely displace the ammonium sulfate in the formulations.

Before initiating laboratory work, it was deemed important to review all literature pertaining to melt and aqueous processes and fertilizer products; to evaluate the status and potential market for sulfur bearing fertilizers; and to review fertilizer usage to determine which grades offer potential for large volume outlets of ammonium sulfate in granular formulation.

Following the literature review, the most promising process and raw materials would be selected. An extensive laboratory evaluation would be made to verify the feasibility of the process and to solve any operating problems which might be found. This laboratory work would incorporate studies of the effects of changes of chemical formulation, of changes of operating conditions and of physical and chemical properties of the materials which would be produced.

The results of the laboratory investigation would be evaluated in a small and a large pilot plant. The small pilot plant would be designed for a capacity of 45 kg/hr. Most of the pilot plant testing would be conducted in this unit. The large pilot plant would be designed for a capacity of 454 kg/hr. It would be used to verify the results of the work in the small unit and to demonstrate the operability of the process by running it continuously for five days.

The data obtained from the laboratory and pilot plant work would be used to design a 227 Mt/d and a 907 Mt/d plant. Capital and operating cost estimates would be prepared for both plant sizes.

At the conclusion of all the work described above, the feasibility of the process would be reviewed. As warranted by the results obtained in this study, recommendations would be developed for further investigation by field tests or by engineering research and development.

BACKGROUND AND THEORETICAL APPROACH

The conventional method of producing granulated fertilizer is by an aqueous process. A flow sheet of a conventional ammoniation-granulation plant is shown in Figure 1. As seen in this figure, the conventional process requires the following major pieces of equipment and steps:

1. Preneutralizer - Phosphoric and sulfuric acids are partially neutralized with ammonia. This step produces much heat and water vapor.

2. Ammoniator-granulator - Partially neutralized acids are ammoniated to the end point. Materials such as potassium chloride and micronutrients can be added at this point. In this step, water vapor and excess ammonia must be recovered or removed.

3. Dryer - Product from the ammoniator-granulator is dried. This step produces much dust and requires a considerable input of heat.

4. Cooler - Product from the dryer is cooled so that it can be handled and stored.

5. Screen - The screening unit separates the dryer product into three fractions: oversize, which is sent to the crusher and recycled; market size, which is sent to the storage bins; and fines, which are recycled back to the ammoniator-granulator.

A conventional granulation plant emits both air and water pollutants. The problem areas and types of pollutants emitted are:

1. Ammoniator-granulator - Dust, ammonia and water vapor, and fine particulate aerosols, e.g. ammonium chloride and fluorides.

2. Product dryer - Dust, water vapor.

3. Product cooler - Dust.

4. Liquid scrubber - Aqueous fertilizer solutions.

In most cases, to control these effluents in existing plants is costly; for older plants it is perhaps prohibitively so.

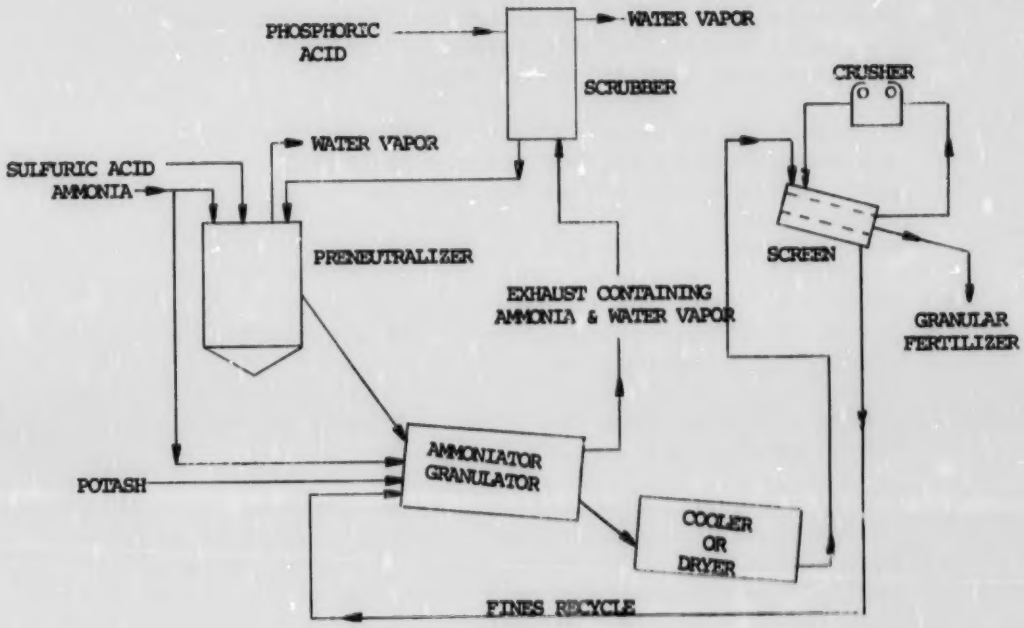


Figure 1. Flow sheet of conventional fertilizer plant.

In the new manufacturing process ammonium phosphate - polyphosphate melt was to be made from proper combination of ammonia and wet process phosphoric acid. This melt was to be mixed with ammonium sulfate and other ingredients, such as potassium chloride, as required by market demand. Ammonium sulfate might comprise up to 55% of the raw material used in the new mixed fertilizer.

The key to the process was considered to be its capability to produce an ammonium phosphate - polyphosphate melt from conventional, merchant grade, wet process phosphoric acid. It was necessary to produce a melt combining two characteristics which had been considered mutually exclusive: polyphosphate content sufficient to provide good temperature and flow characteristics, and the capability to solidify and granulate readily in combination with ammonium sulfate at low recycle rates. This melt was to be produced by reacting ammonia with phosphoric acid under conditions similar to those used in anhydrous productions. The sensible heat of the feedstock plus the exothermic heat of reaction would be utilized to evaporate all the free water and a controlled portion of the chemically combined water.

Ammonium polyphosphate melt, water, ammonium sulfate and potassium chloride were to be combined in a pan-type granulator, a Tennessee Valley Authority (TVA) ammoniator, or a pug mill -- as was used in this investigation -- to form hard, round fertilizer granules. It was hoped that it would prove possible to produce medium and high analysis fertilizer grades when the ammonium phosphate - polyphosphate melt was concentrated and the total mixture had a low water content. (The low nitrogen content of ammonium sulfate naturally limits the total nutrient content of the N-P-K mixtures which can be produced. However, when sulfur is required by the crop and the soil, ammonium sulfate becomes a high nutrient carrier.)

Two basic processes were developed. A discussion of the selection criteria for each of the major process steps is presented in Section V of this report.

DESCRIPTION OF PROJECT PHASES

A description of each phase and a brief description of the tasks involved is presented below.

Phase I - Laboratory Optimization

The laboratory optimization consisted of the tasks outlined below.

Task 1. Literature Review - A search was conducted of all Ferguson Industries' ammonium phosphate and ammonium polyphosphate process and product information, of technical information from the TVA and universities, and of industrial research and development literature. The compiled information was used to select the most promising production process and raw materials for laboratory evaluation and pilot plant design.

Task 2. Selection of Fertilizer Compositions and Processes - A market analysis was undertaken to determine the types and quantities of fertilizers currently used in each region of the United States. This was done to determine desired chemical compositions of the new fertilizer products, the standard processes used to make the various fertilizer grades and fertilizer plant pollution sources and control techniques.

Task 3. Laboratory Testing - A program was carried out to establish the effects of ammonium polyphosphate concentration, ammonium sulfate grade and potassium chloride concentration on the fertilizer product quality. Process steps evaluated in the laboratory included mixing techniques, thermal treating and atmospheric control.

Task 4. Measure Fertilizer Quality - Fertilizer quality was determined by laboratory tests of nutrient analysis, solubility, storability and granule quality. Agronomic testing was not a goal of this effort, but was left for future evaluation.

Phase II - Pilot Plant Design and Construction

Two pilot plants were designed and constructed. The smaller plant, in which most of the experiments were conducted, had a capacity of 45 kg/hr (100 lb/hr). Process information and product quality data obtained by operation of this unit were used as the basis for design of the larger 454 kg/hr (1000 lb/hr) pilot plant. Tasks outlined below were essentially similar for both plants.

Task 1. Preliminary Design and Instrumentation - Results obtained in the Phase I work were used to establish chemical process steps, raw materials and handling operations to be tested in the pilot plants. Equipment sizing and a tentative process flow sheet for the plant were established. This preliminary process design was used as the basis for the mechanical design and equipment selection of Task 2. Instrumentation required for process control and monitoring of plant operations was defined.

Task 2. Mechanical Design and Equipment Selection - The pilot plant was designed and drawings were made. Equipment and instruments were selected.

Task 3. Release of Purchase Orders for Equipment and Components - Purchase orders for equipment, components, instruments and supplies were issued. Manufacturing instructions for subsystems fabricated by Ferguson Industries were provided. Raw materials for the pilot plant were ordered.

Task 4. Receipt of Parts, Equipment and Components - Purchased parts, equipment, instruments, components and in-house fabricated subsystems were received. Raw materials for pilot plant operation were received and stored.

Task 5. Construction and Assembly of Pilot Plant - The pilot plants were constructed.

Phase III - Pilot Plant Operations and Analysis

For each pilot plant operation, the tasks were:

Task 1. Pilot Plant System Check - All subsystems of the pilot plant were checked separately and in combination for proper operation and function. Debugging and redesigning were performed as required.

Task 2. Pilot Plant Start-Up - The pilot plant was put in operation and individual plant process steps were checked for proper operation.

Task 3. Pilot Plant Operations - The pilot plant was operated at various production rates and with various combinations of raw materials. Parameters significantly affecting production costs and fertilizer product quality, as well as plant effluent and emission levels, were used. Plant modifications were made as required. The small pilot plant was operated for four months, and the large one for about sixty days.

Task 4. Analysis of Pilot Plant Products, Operation and Effluents - The fertilizers produced at various operating modes of the plants were analyzed for the following characteristics:

1. Polymerization Levels (Non-orthophosphate concentration)
2. Feed Stock Ratios
3. Feed Stock Grades
4. Solubility
5. Storability
6. Granule Quality

The effluents and emissions from various sources were sampled and analyzed.

PHASE IV - Best Chemicals - Process Selection and Scale-Up to Full Sized Plant

This phase consisted of three tasks, outlined below:

Task 1. Best Chemicals - Process Selection and Flow Diagram - Results from the laboratory and pilot plant phases were analyzed in terms of project goals. The optimum process flow sheet and raw materials were selected on the basis of this analysis.

Task 2. Scale-Up to Full Scale Plant - All previous work results were used to perform the scale-up to full scale plant design. Final flow sheets were generated. Plant components, instrumentation and subsystems were sized. Drawings of the plant layout were made. This full scale plant design was used in the cost-effectiveness analysis of Task 3.

Task 3. Cost-Effectiveness Analysis - The prices of raw materials, plant capital investment, labor, overhead and other financial factors were analyzed. Costs were compared for production of the new fertilizer in new plants and in typical remodeled plants. Costs were compared for melt and aqueous produced granular fertilizer of the same grade.

SECTION II

CONCLUSIONS

1. A process was developed in which ammonium phosphate - polyphosphate melt technology was utilized to produce a high concentration granular fertilizer containing a major proportion of waste or by-product ammonium sulfate. The process was successfully tested in a continuously operated 454 kg/hr demonstration unit.

2. The type of pollutants generated by the process can be readily contained by the utilization of known technology; the quantity of pollutants is significantly less than would be produced in a plant using an aqueous process to produce the same fertilizer grades.

3. This new technology offers lower capital and operating costs than other procedures for incorporating large quantities of solid ammonium sulfate into mixed fertilizer granules.

4. The process can be readily adopted by existing granulation plants.

5. Utilization of the process would tend to enhance the market for by-product and waste ammonium sulfate.

6. Most of the processes now recommended for scrubbing sulfur dioxide from power plant stacks do not recover sulfur in a form which can be used for agricultural purposes. If an ammonia scrubbing process were adopted, then sulfur dioxide would be converted into ammonium sulfate. As indicated above, the ammonium sulfate could readily be incorporated into a granular fertilizer.

7. Agriculture in the United States is operating on a negative sulfur balance. The addition of sulfates to mixed granular fertilizers will be helpful, particularly in those areas in which soil sulfur deficiencies have been reported.

SECTION III

RECOMMENDATIONS

Based on competitive price structure and pollution benefits to be derived from the proposed manufacturing process and the demonstrated capability of the pilot plant to produce quality products, it is recommended that:

1. A 227 metric ton per day (250 short ton per day) prototype plant be built and operated to demonstrate the process on a large scale and to establish the most cost-effective method of operation.

2. Agronomic tests be made to determine field response to the use of the fertilizers. Such tests should be made particularly in areas where examination of soil or of plant tissues has shown the soil to be deficient in sulfur. Crop responses should be studied to determine whether there are any trace elements in the by-product or waste product ammonium sulfate which affect plant growth adversely.

3. Laboratory tests be initiated to determine the possibility of modifying the newly developed fertilizers to impart slow release properties to them. It may be possible to accomplish this by incorporating certain materials within the fertilizer or by using such materials as coating agents. Products which have been suggested as suitable for this purpose include wax, sulfur and plastic substances.

SECTION IV

LABORATORY INVESTIGATION

PREVIOUS WORK

All previous work performed by Ferguson Industries in ammonium phosphate and ammonium polyphosphate processing, technical information from TVA, the Environmental Protection Agency and universities, and industrial research and development were searched to avoid any duplication of effort. The search was expanded to include all studies which utilized ammonium sulfate, ammonium polyphosphate, potassium chloride and admixtures of these. Conclusions drawn from this research provided a basis for tentative selection of the most promising production process and raw materials. At the same time, tentative selection was made of plant process steps and raw materials which would minimize environmental pollution. Current knowledge of processes, chemical mixtures and production techniques is summarized below.

Ferguson Industries and others[1] have noted that a melt of ammonium polyphosphate can be mixed directly with ammonium sulfate and potash to avoid several manufacturing steps which consume energy, require capital investment and are major sources of pollutants. This consideration led to the conclusion that ammonium phosphate - polyphosphate is the best material, on balance, to use for direct combination with ammonium sulfate to produce a good, mixed fertilizer. A further advantage of such granulated phosphatic fertilizers is their lack of low melting constituents. This characteristic enables them to be coated with water-insoluble substances such as waxes, asphalt and sulfur for conversion into slow release substances.

The technology of polyphosphates has been developed primarily for the production of fertilizer liquids. The range of polyphosphates in liquid fertilizers is usually 70% or higher.

It has been found that solid fertilizers which contain large concentrations of polyphosphates are primarily amorphous in nature and exhibit cold flow characteristics. They have poor manufacturing, handling and storage properties. Up to this time, no acceptable solid

product containing over 50 percent (50%) polyphosphates has been found. TVA has produced solid products containing up to 50% polyphosphates in commercial demonstration plants. Most commercially acceptable fertilizers contain less than 25% polyphosphates.

High order, single species potassium polyphosphates with slow release properties have been produced. While these compounds are available commercially, there is no reported method for their direct production by reaction of anhydrous ammonia and phosphoric acid.[2,3] High fugacity of ammonia appears to be the impediment to development of a commercial process.

Liquid fertilizers generally are produced from anhydrous ammonia and superphosphoric acid containing appreciable quantities of polyphosphates. Direct reaction of these two materials produces temperatures over 300 degrees Centigrade (570 degrees Fahrenheit).

Merchant grade wet process phosphoric acid containing 52 to 55% phosphorus pentoxide (P_2O_5) also can be reacted directly with anhydrous ammonia to produce fertilizers containing 15 to 55% polyphosphates. Reaction temperatures will be above 200° C (390° F). Fertilizers with a wide range of polyphosphate content can be produced by manipulation of process variables such as temperature, pressure, retention time and free water content of the reactants.[4,5,6,7] Several variations of this process are noted below.

1. A process test was described which produced polyphosphates at an ammonia:phosphoric acid ratio of 1.6:1.0, a pressure of 0.70 kilograms per square centimeter (10 pounds per square inch), temperatures of 293 to 315° C (560 to 600° F), and residence time of less than one second.[8]

2. Another test produced an ammonium potassium hydrogen phosphate in a bench scale reactor with the following parameter ranges: potassium: phosphorus ratio of 0.5:1.0, temperatures of 200 to 210° C (390 to 410° F), pressures greater than 2.81 kg/sq cm (40 psi) and retention time greater than four minutes. The product contained a polymerized product up to the tripolyphosphate level. Effects of temperature, pressure and retention time were studied.

3. Similar processes are described in which urea is reacted and/or mixed with polyphosphates. Upon being heated, urea will either break down to ammonia and carbon dioxide or react with acid to produce urea - phosphates and ureapolyphosphate.[10,11,12]

A process has been patented in which urea is mixed with ammonium polyphosphate. The range of ammonium polyphosphate content was 25 to 98% of the total P_2O_5, and the urea to ammonium phosphate weight ratio range varied from 85:15 to 25:75.

4. TVA and others have reacted ammonia and phosphoric acid in various concentrations. Ammonium sulfate, urea and potassium salts have been incorporated into the reaction product to form a variety of fertilizers.[1,13,14,15,16] None of these fertilizers was considered to have slow release properties.

5. An accidental water loss during the operation of one of Ferguson Industries' super-acid fertilizer plants in Georgia resulted in the plugging of the reactor column with an ammonium phosphate solid containing substantially more polyphosphates than the feed acid. In September 1968, this observation led Ferguson Industries to build a crude pipe reactor to test the theory of direct ammoniation of phosphoric acid to produce polyphosphates.

   The reactor consisted of a 2.54 cm (1 inch) diameter pipe approximately 1.8 M (6 feet) long with an aspirator jet attached to one end. The motive power for the aspirator was 427° C (800° F) ammonia at 7 kg/sq cm (100 psi). Boiling ortho acid was introduced into the jet by aspiration only. The ammonium phosphate - polyphosphate melt was discharged into a container of water. This first attempt at direct ammoniation netted a product containing 9% nitrogen and 62% P_2O_5 with a polyphosphate content of 75.77%. In order to aspirate 0.5 kg (1 pound) of acid in this crude system, it was necessary to use 3.0 kg (6 pounds) of heated ammonia.

   Many pilot plant modifications were made in late 1968 to develop an efficient and controllable operation. In February 1969, a series of pilot plant test runs was made to establish the parameters affecting formation of polyphosphates. It was concluded that polyphosphate formation was highly dependent upon reaction temperatures and feedstock concentrations, as shown in Figure 2.

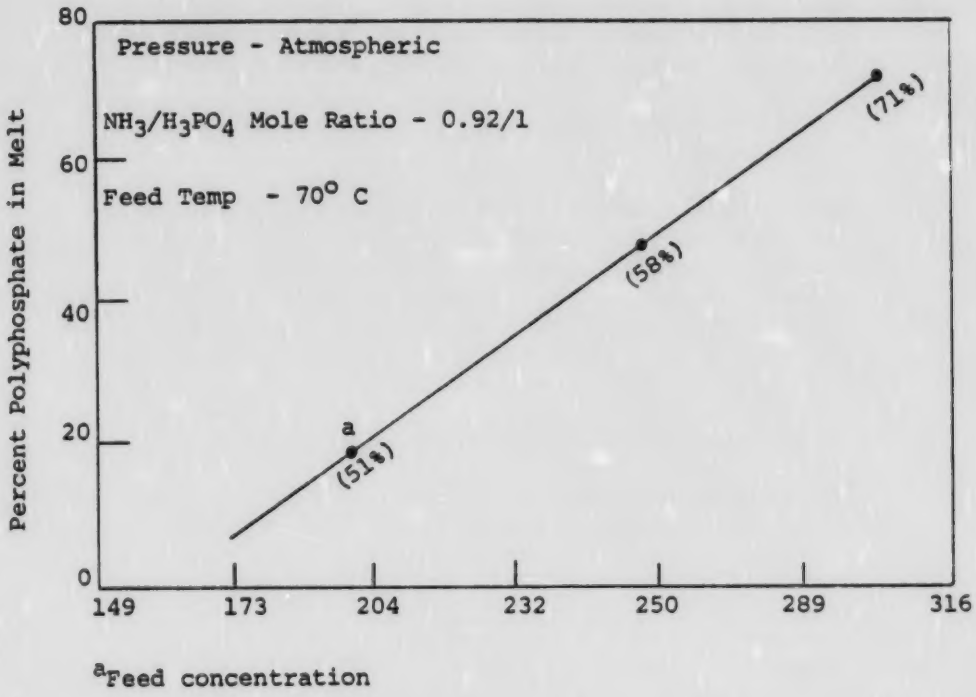


Figure 2. Polyphosphate concentrations vs. reaction tube temperature.

Analysis of the product melt showed particular consistency in the 12% N and 58% P_2O_5 range. Several product characteristics were observed. The polyphosphate hydrolyzed rapidly unless the melt was cooled below 125° C (255° F) within five to fifteen minutes. Also, hydrolysis would occur upon addition of very small quantities of water. The polyphosphate concentration of the melt was critical to successful crystallization. If the polyphosphate concentration was above 40% the melt would remain plastic, sticky and soft rather than crystallize.

6. The use of ammonium polyphosphate as a carrier for micronutrients is well documented by TVA and others.[17,18,19] Ammonium sulfate has been mixed with ammonium polyphosphate to produce a high sulfur content material.[20,21,22]

7. Much data have been produced on the comparative effects of ammonium polyphosphate and ammonium phosphates on plant growth and production. All reports show that ammonium polyphosphates are effective to an equal or greater extent than the orthophosphates. Economic comparisons of the two fertilizers show that the polyphosphates are preferred for their higher concentration of plant nutrients per unit volume.

LABORATORY STUDY

A laboratory scale granulation and product quality study was performed to determine various chemical and physical parameters of production and product quality. Raw materials were combined in various proportions under different mixing conditions to determine the optimum set of variables for production of the fertilizer grades and qualities shown most desirable in market analysis.

Critical Process Factors

As both laboratory and plant experience have demonstrated, it is impossible to retain ammonia in ammonia to phosphoric acid mole ratios greater than one in the melt granulation system. Mole ratios less than one result in products which contain free acid and exhibit poor storage and handling characteristics. Therefore, for any nutrient formulation, the amounts of ammonia and phosphoric acid are fixed by the desired P_2O_5 content. Thereafter, ammonium sulfate may be added to bring the

nitrogen content of the fertilizer to a desired level; potassium chloride may be added to bring the potassium to a desired level; and an inert filler may be used to complete the fertilizer analysis. Thus, the amount of nutrients required for any given analysis is fixed.

One of the most important considerations in the melt granulation process is the necessity of having a sufficient quantity of melt to serve as a bonding agent for the solid ingredients in order to form a hard, stable granule. In low melt formulations, those containing high concentrations of ammonium sulfate or potash, it is absolutely essential that the mixing action produce a high yield of product-size granules so that the recycle ratio is held to a manageable level, because the recycled material acts, in essence, like any other solid material. If the ratio of melt to recycle becomes too low, there will be an insufficient amount of bonding agent to form granules and the process will become inoperable.

In this regard, the melt process, with its fixed amount of nutrients for any given fertilizer analysis, is less flexible than the aqueous process. In the latter process, it is possible to add more water when necessary, thereby increasing the quantity of the bonding agent.

Laboratory work was directed to the development of melt processes by which phosphoric acid, ammonia, ammonium sulfate, potash and filler, if needed, could be formed into a commercially acceptable granular product. The variables which were studied included:

1. Concentration and impurity level of phosphoric acid.

2. Temperature of phosphoric acid and of ammonia piped to the reactor.

3. Reaction temperature.

4. Melt (reaction product) solidification temperature.

5. Temperature of undersize recycled to granulator.

6. Temperature of ammonium sulfate, potassium chloride and filler added to the granulator.

7. Particle size of ammonium sulfate and potassium chloride added to the granulator.

8. Granulator holding time.

Laboratory Procedures

The solids-melt combinations were produced by two techniques:

1. Ammonium phosphate - polyphosphate particles were remelted in the laboratory and granulated with the solids in a Hamilton-Beach mixer.

2. Melt was produced in a small tee reactor and directed onto the agitating bed of solids in the Hamilton-Beach mixer.

Although these test data were reported separately, the results were similar and only one set of conclusions was reached.

Test Results

The results of selected tests are reported in the Appendix, Section IX, in Table A-1 and text. The laboratory work indicated that the proposed process was technically feasible.

The conclusions of the laboratory work may be summarized as follows.

Grade of Fertilizer - The concentration of ammonium phosphate melt in the mixed product was varied. Eight different concentrations of melt, ranging from 11.00 to 54.73% by weight of mix, were combined with dry solid ammonium sulfate and potassium chloride. Table 1 shows the material ratios for the various fertilizer grades which were produced.

The laboratory work was concentrated on the 13-13-13-13 grade for the following reasons:

1. The 1-1-1 ratio is one of the major grade ratios used by the farmer.

2. By inspection of Table 1, it is apparent that this grade contains the highest concentration of ammonium sulfate, more than 50%.

3. Because the ratio of dry solids to melt in this grade is the highest of all major fertilizer ratios, it is the most difficult to produce by the melt granulation process.

Table 1. MATERIAL RATIOS OF POTASSIUM CHLORIDE, MELT (AMMONIUM PHOSPHATE) AND AMMONIUM SULFATE TO PRODUCE VARIOUS FERTILIZER GRADES

Grade	kg/Mt[a]	lb/t[a]	Ingredients	Solid/Melt
16-31-0-11	544	1088	Melt[b]	0.84
	451	902	Sulfate[c]	
14-42-0-6	737	1474	Melt	0.35
	246	492	Sulfate	
14-24-12-9	193	386	Potash[d]	1.37
	420	840	Melt	
	387	774	Sulfate	
14-24-10-12	161	320	Potash	1.37
	420	840	Melt	
	387	774	Sulfate	
14-24-8-11	130	260	Potash	1.39
	420	840	Melt	
	387	774	Sulfate	
13-13-13-13	210	420	Potash	3.34
	225	460	Melt	
	489	980	Sulfate	
13-30-10-8	161	332	Potash	0.92
	525	1050	Melt	
	319	638	Sulfate	
12-24-12-13	420	840	Melt	1.98
	330	840	Sulfate	
	194	388	Potash	

[a]Difference between 1000 kg and/or 2000 lb adjusted by addition of filler, where necessary.

[b]Ammonium phosphate melt, 12-57-0.

[c]Ammonium sulfate, 21% nitrogen.

[d]Potassium chloride, 62% (K_2O).

Concentration of Polyphosphates in the Melt - Early studies indicated that degrees of polymerization of phosphates in the melt might have an effect on granulation. Therefore, different melt phosphate concentrations, varying from 12.5 to 55.6% polyphosphate based on the total phosphate content, were tested. Summarizing data are shown in Table 2.

It was found that good granulation, evidenced by the production of hard granules, was obtained repeatedly with up to 35.6% poly concentration when fine mesh (-40) ammonium sulfate was used. However, when coarse mesh (-14 to +40) ammonium sulfate and/or potassium chloride was mixed with high polyphosphate content melt, more irregular fertilizer granules were produced. It was concluded that the optimum concentration for obtaining consistently good granulation is approximately 25% polyphosphate.

Concentrations of Ammonium Sulfate in the Mixed Product - The initial tests utilized a low ratio of solids to melt and, therefore, low concentrations of ammonium sulfate. Successful granulation was achieved although granule quality was unsatisfactory. Other investigators have reported similar results.[1,2,3]

As noted previously, the objective of this investigation was to develop a process that would offer large market outlets for by-product ammonium sulfate and would produce popular fertilizer grades with high nitrogen ratios. The fertilizer grade which contains the most ammonium sulfate, approximately 54%, is 13-13-13-13. The first laboratory tests designed to adapt the melt technology to the granulation of this grade were not successful. It was found necessary to apply standard aqueous technology to produce satisfactory granules.

Various polyphosphate concentrations were tried. The polyphosphate levels of the melt were attained either by heating an intermediate concentration of phosphoric acid and ammonia prior to reaction, or by using a more concentrated phosphoric acid. Reaction temperature is a function of product polyphosphate content. It was observed that polyphsphate melt tended to agglomerate within itself and not to incorporate any of its solid constituents into the granules.

As polyphosphate content was lowered, melt viscosity decreased. The melt dispersed more readily. The effect was the same as if the melt-to-solids ratio had been increased. However, although the polyphosphate level was dropped progressively to zero, it still was impossible to obtain satisfactory granulation.

It was found necessary to utilize an aqueous solution to achieve successful granulation. Such granules had to be dried to attain satisfactory storage and handling properties.

Table 2. POLYPHOSPHATE CONCENTRATION IN PRODUCT AND GRANULATION QUALITY

Sample Number	Analysis, %				Temp., °C		Phosphate, %		Granulation	Comments
	Melt	KCl	AS	Fine	Solid	Melt	Total	Poly		
11-17	24.55	22.55	52.89	52.89	260	191	13.4	20.4	good	Hard, melt conditioned with NH_4OH, then heated.
11-16	24.55	22.55	52.89	52.89	177	232	15.5	25.3	good	Very hard melt; conditioned with NH_4OH.
12-15	19.60	18.00	42.40	20.00	-	-	20.49	31.2	-	Low attrition, pH 2.7.
10-31	23.0	24.00	52.00	-	177	-	21.14	30.8	good	Good sample.
12-15	24.55	22.55	52.89	52.87	163	218	17.37	35.0	good	Attrition 19%.
10-31	23.00	24.00	52.00	-	121	-	13.45	34.0	-	Added melt to dry elements, bad mixing.
11-21	24.55	22.55	53.00	75.55	204	204	13.90	37.2	good	Attrition 3.93.
12-12	24.55	22.55	52.29	52.89	163	191	16.71	38.1	fair	Without NH_4OH.
12-13	46.85	43.04	10.09	53.13	163	204	16.12	41.3	good	Ammonium sulfate ground.
11-03	24.70	22.10	53.20	53.20	163	246	16.41	42.3	good	
11-15	24.70	22.09	53.21	53.21	163	246	18.48	43.2	v. poor	Mixed melt with NH_4OH - heated.
11-21	24.55	22.55	53.00	22.55	-	-	15.34	45.2	poor	Excessive melt.
11-22	24.55	22.55	53.00	53.00	204	204	14.49	45.9	good	
11-22	24.55	22.55	53.00	None	177	204	13.60	51.1	poor	Slow cooling, 21.08% attrition.
11-16	24.55	22.55	52.89	52.89	177	260	14.64	52.5	good	Mixed melt with NH_4OH, then heated.
12-14	24.55	22.37	53.46	75.83	163	204	15.88	53.3	poor	Soft.
11-14	24.55	22.55	52.89	31.20	163	246	15.97	55.6	v. good	KCl -14 to 40, 88.3%.
02-21	24.55	22.55	52.89	52.89	177	204	26.03	12.5	good	High pH, very hard.

Table 2. (Continued) POLYPHOSPHATE CONCENTRATION IN PRODUCT AND GRANULATION QUALITY

Sample Number	Analysis, %				Temp., °C		Phosphate, %		Granulation	Comments
	Melt	KCl	AS	Fine	Solid	Melt	Total	Poly		
02-21	24.55	22.55	52.89	52.89	177	204	19.42	13.0	good	Better granulation.
02-08	24.55	22.55	52.89	52.89	191	204	22.18	14.0	-	Many fines, mainly KCl, agglomerate melt, pH 2.8.
02-22	24.55	22.55	52.89	52.89	177	213	20.61	14.5	-	Melt at 250 cooled too fast; temp. of melt 350°.
02-22	24.55	22.55	52.89	-	191	218	20.81	20.7	v. good	High pH.
02-24	24.87	23.24	49.64	-	177	210	17.83	20.8	-	Temp. of melt 350°, over-agglomeration, pH 4.3.
02-24	24.55	22.55	52.89	52.89	191	204	20.00	21.5	v. good	Over-agglomeration, 9.02 attrition, pH 4.7.
02-27	24.55	22.55	52.89	-	191	216	14.49	23.7	-	KCl +20 mesh, pH 4.2.
02-28	24.55	22.55	52.89	-	163	204	14.19	24.2	-	KCl +20 mesh, pH 4.0; irregular, angular granules.
03-19	24.55	22.55	52.89	-	160	246	15.37	24.8	-	pH 3.1.
02-21	24.44	22.55	52.89	52.89	204	204	12.84	25.6	none	pH 4.5.
02-24	24.87	23.24	49.64	49.64	191	199	22.77	25.9	-	Over-agglomeration, pH 4.0, 2.25% urea.
03-05	24.55	22.55	52.89	26.45	191	210	14.19	26.3	good	Agglomerate of AS and KCl, KCl not completely wetted; pH 4.8.
02-28	24.55	22.55	52.89	52.89	199	216	14.49	28.9	good	Solid too hot, much oversized particles 36.6%.
02-28	24.55	22.55	52.89	52.89	-	-	14.49	28.0	-	pH 4.5.
03-05	24.55	22.55	52.89	13.22	191	216	14.34	29.2	good	Solid too hot or too much melt, pH 4.4.
02-24	24.87	23.24	49.64	49.64	204	204	12.78	36.0	-	Too hot, pH 4.5, 2.25% urea.
03-19	24.55	22.55	52.89	26.45	193	246	15.66	38.3	-	pH 3.4.
03-19	24.55	22.55	52.89	13.72	193	246	15.08	29.8	-	pH 3.5.

At this point, it may be desirable to point out that at atmospheric pressure the ammonia-phosphoric acid-water system behaves differently than either the ammonium nitrate-water or the urea-water system. The latter two systems maintain a single liquid phase as they are heated, and the water content of the solution is decreased from 100% down to 0%. The ammonia-phosphoric acid-water system, at a one-to-one mole ratio of ammonia to phosphoric acid, is discontinuous from about 40 or 45% down to 0% water. In this discontinuous range, a two phase system is formed, consisting of a liquid plus solid mono-ammonium phosphate. Therefore, when an aqueous solution is employed in a granulation process, the liquid binder always contains approximately 40% water. The removal of this water would require additional processing steps and the expenditure of energy. Such costs were considered inconsistent with project goals.

Heating of the solid ingredients was tried next. It was found that heating these materials above the crystallization point of the melt brought about a remarkable transformation. At this temperature, the particles were wetted by the melt. Upon subsequent cooling and crystallization, hard, stable granules were formed.

Some flexibility is needed in plant operations to compensate for the amount of recycle or for other operating contingencies. This can be attained by changing the polyphosphate content of the melt, utilizing either of the two methods mentioned above. The result would be the same as if the ratio of melt-to-solids had been changed.

Source Grades of Ammonium Sulfate Used - Samples of by-product ammonium sulfate were obtained from four suppliers. Physical characteristics are listed in Table 3. Coarse and fine mesh particles from both the chemical and steel industries were used. Fine mesh ammonium sulfate generally is the most difficult to market by these industries. Chemical characteristics of the by-product ammonium sulfate obtained from various sources differed only slightly and required no concentration adjustments to produce the same fertilizer grades.

Concentration of Potassium Chloride in the Mixed Product - Six potassium (chloride) gases were made, as indicated in Table 1. It was observed that the behavior of potassium chloride in the melt system was very similar to that of ammonium sulfate. As before, it was found necessary to heat the potassium chloride crystals to obtain satisfactory wetting by the ammonium phosphate melt and to produce good granules.

Granulator Mixing Temperature - Each grade has an optimum range of granulation temperatures. For example, the best temperature range for granulation of grade 13-13-13-13 is 175 to 200° C (345 to 390° F), as shown in Table 4, whereas grade 13-30-10-8 can be granulated sucessfully at 100 to 160° C (210 to 320° F).

Table 3. SCREEN ANALYSIS OF SOURCES OF AMMONIUM SULFATE
(Cumulative percent by weight)

Mesh No. (U.S. Std.)	International Minerals & Chemicals Corp.	Weirton Div. Of National Steel Company	Jones and Laughlin Steel Company	Dow-Badishe Company
12	-	12.4	20.1	-
14	-	30.3	-	13.8
20	1.7	83.0	77.5	58.0
30	-	-	97.0	-
40	40.0	96.6	-	88.0
50	-	-	99.4	-
70	-	-	99.4	-
100	95.0	-	-	99.0
-100	5.0	-	-	-

Table 4. MIXING TEMPERATURE/RECYCLE EFFECT ON GRANULATION (Grade 13-13-13-13)

Sample Symbol	Analysis, %					Temperature, °F		Granulation Quality	P, as PP, %	Comments
	$N-P_2O_5-K_2O$	Melt	KCl	AS	- 14 Mesh	Solid	Melt			
11-15-2	12-57-0	24.7	22.1	53.2	53.2	325	475	v. poor	43.2	Mixed melt with NH_4OH; heated.
11-16-2	12-57-0	24.6	22.6	52.9	75.4	325	450	v. poor	--	Mixed melt with NH_4OH; heated, solid not wet.
	12-57-0	24.6	22.6	52.9	52.9	350	350	good	52.5	Mixed melt with NH_4OH; heated, 58% marketable.
	12-57-0	24.6	22.6	52.9	52.9	350	450	good	25.3	Melt conditioned with NH_4OH, very hard.
11-17-2	12-57-0	24.6	22.6	52.9	52.3	500	375	good	20.2	Melt conditioned with NH_4OH, heated; hard, 53% marketable.
11-14-2	--	--	--	--	--	325	400	--	--	Ammoniated a sample that was very sticky, stayed sticky.
01-04-3	11-60-0	18.7	17.3	40.3	40.3	300	425	good	--	pH 5.0 - 5.5; ammoniated after granulation.
	11-60-0	18.7	17.3	40.3	40.3	275	325	good	--	pH 3.5; ammoniated during granulation.
01-09-3	12-57-0	19.6	18.0	42.2	42.2	250	425	good	--	pH 4.5; ammoniated.
01-12-3	--	24.6	22.6	52.9	52.9	--	--	rubbery	--	Lab melt, acid + NH_4OH.
01-15-3	--	24.6	22.6	52.9	52.9	375	250	good	--	Lab melt, acid + NH_4OH.
02-07-3	12-57-0	12.3	11.3	26.5	26.5	225	425	v. good	--	Added acid to melt before granulation.
	12-57-0	12.6	11.3	26.5	26.5	225	425	none	--	Added acid to solids before heated.
02-24-0	--	24.8	23.2	49.6	0.0	--	410	--	--	pH 4.3, over agglomeration, much fines, 36% marketable.
	--	24.8	23.2	49.6	49.6	400	400	--	--	pH 4.5, too hot, some granulation achieved by crushing hot.

As a general rule, the higher the solids-to-melt ratio, the higher the required granulation temperature. The ratio of recycled material to product also affects the granulation temperature. As the recycle ratio is increased at a high solids-to-melt ratio, it becomes necessary to increase the granulation temperature. This is not true when the solids-to-melt ratio is low. In this case, the optimum granulation temperature may be either high or low, and the operator must observe the process to make the proper adjustment. When insufficient granulation is noticed, the process is corrected by increasing the granulation temperature; when excess fluidity is noticed, the process is corrected by decreasing the temperature.

Granulator Mixing and Crystallization Technique - The granulator has two functions: to mix the melt with the solid constituents, and to effect a phase change of the melt.

Thorough mixing of the melt with the solid ingredients with which it is to be incorporated occurs while the materials are still hot.

Heat must be removed before crystallization can occur. Normally, this is done by air cooling. However, in the course of these experiments it was found that heat could be removed more advantageously by adding cold raw materials to the mixture of melt and recycle. Most of the raw materials do not agglomerate at this time, but they do remove the heat of crystallization of the mixture. The unagglomerated materials are separated on the product screen and returned as recycle. The advantage of this procedure is that the cost of air blowing is reduced significantly; the energy and equipment needed to heat the raw materials is decreased or eliminated; and the requirement for pollution control is signally reduced.

Particle Size Effects of Ammonium Sulfate and Potassium Chloride on Granulation - Because the size of dry mix materials used in the process cannot always be specified, the effect of variations of particle size of the ammonium sulfate and potassium chloride dry mix materials on the granulation quality and marketable fraction of the product was investigated. Only a 13-13-13-13 grade, with the lowest melt-to-solid ratio, was studied; the melt must wet more solids for this formulation than for any other. Formulation "fines" are defined as that portion of the mixed chemicals passing the No. 14 screen. Test results indicated that for a high quality granule and a high percent marketable product, optimum fines, at the mixed temperatures utilized, are about 50% by weight of the total amounts added. Efficiency decreases at more or less than this figure. Summary data are presented in Table 5.

Table 5. PARTICLE SIZE EFFECT OF AMMONIUM SULFATE AND POTASSIUM CHLORIDE ON GRANULATION (Grade 13-13-13-13)

Sample Symbol	Analysis, %					Temperature, °F		Granulation Quality	% Marketable	Comments
	Melt N-P_2O_5-K_2O	Melt	KCl	AS	- 14 Mesh	Solid	Melt			
10-24-2	12-57-0	24.2	22.4	52.5	52.5	75	--	poor	--	Over agglomeration and unagglomerated material.
11-14-2	11.5-61-0	24.6	22.6	52.9	31.2	325	475	v. good	55.7	KCl 88% -14 +40.
12-13-2	12-57-0	46.9	53.0	10.0	43.0	325	300	good	59.1	--
11-21-2	12-57-0	24.6	22.6	53.0	75.6	400	400	good	43.7	Granulation 30 seconds.
11-21-2	12-57-0	24.6	22.6	53.0	22.6	--	--	poor	41.7	Excessive melt.
11-22-2	12-57-0	24.6	22.6	53.0	53.0	400	400	good	64.4	--
11-22-2	12-57-0	24.6	22.6	53.0	none	350	400	poor	45.2	Slow cooling; 21% (-14 mesh).
12-12-2	12-57-0	24.6	22.6	52.9	52.9	325	275	fair	54.4	--
12-13-2	12-57-0	46.9	43.0	10.1	53.1	325	400	good	59.1	--
12-14-2	12-57-0	24.4	22.4	53.5	75.8	325	400	soft	33.1	Rounded particles; KCl and AS added for heat transfer.
12-14-2	12-57-0	24.3	22.4	53.5	75.8	325	40	poor	--	Very sticky.
12-15-2	12-57-0	24.6	22.6	52.9	52.8	325	425	good	31.0	19% attrition.
01-12-3	--	24.6	22.6	53.0	53.0	--	--	none	--	Rubber-like product melt produced in lab.
01-15-3	--	24.6	22.6	53.0	53.0	375	250	good	--	pH high; melt produced in lab.
01-15-3	12-57-0	24.6	22.6	53.0	--	--	--	--	--	--

Recycle Effects on Granulation - Table 6 summarizes data on recycle effect for grade 13-13-13-13 product at approximately the optimum granulation temperature. The data indicate that the recycle rates for good granulation generally are less than 30%. The marketable portions of the product reported in Table 6 are representative of the complete data set.

Pertinent Physical Characteristics - Several laboratory tests investigating reaction to moisture were performed. These tests included:

Hygroscopicity - Table 7 shows the results of hygroscopicity tests on on two general grades of product. The Ferguson research product shows higher moisture absorption than the conventional Olin product. However, these results may not be as truly indicative of caking sensitivity as they purport to show. Samples of Ferguson product made in the research pilot plant, having been stored at warehouse conditions for over a year, are still free flowing and show no evidence of caking.

A possible explanation of this behavior may be that the polyphosphate in the research product acts as an internal dessicant. Water absorbed from the atmosphere will first convert the polyphosphate to the orthophosphate. It is only when additional amounts of water have been absorbed that the granules become subject to caking. The Olin product does not contain any polyphosphates.

As supporting evidence for this supposition, one may cite the fact that some granular ammonium nitrate is marketed on this basis. Imperial Chemical Industries mixes ammonium nitrate with magnesium nitrate. The latter is an extremely hygroscopic substance which forms a hydrate with six water molecules. When added to the granulated ammonium nitrate, it acts as an internal dessicant.

Critical relative humidity at 30° C (86° F) - Table 8 presents test data attempting to quantify moisture sensitivity of the product by vapor pressure measurements. Results are erratic and do not correlate well with the hygroscopicity results. Thus, it appears that the two different fertilizer products will require different test limits to indicate caking susceptibility.

Relative rates of solution - Table 9 presents comparative data on nutrient solubility. These data indicate that the solubility rates of the Ferguson research products and the Olin products are similar.

Table 6. RECYCLE EFFECT ON GRANULATION AT OPTIMUM TEMPERATURE (Grade 13-13-13-13)

Sample Symbol	Analysis, %						Temperature, °F		Granulation Quality	Mesh -5 +14, %	Comments
	Melt NP_2O_5-K_2O	Melt	KCl	AS	Recycle	- 14 Mesh	Solid	Melt			
12-12-2	12-52-0	17.3	15.9	38.1	26.7	38.1	325	400	good	44.4	--
12-14-2	12-52-0	12.3	11.3	36.0	50.0	37.8	325	400	poor	51.7	Very sticky, (hi-poly).
12-19-2	12-57-0	14.7	13.5	31.7	39.9	31.7	375	375	poor	35.2	pH 2.8; part of recycle not wetted.
01-04-3	11-60-0	18.7	17.9	40.3	23.8	40.3	300	425	good	43.6	pH 5.0 - 5.5; ammoniated with vapors after granulation.
01-04-3	11-60-0	18.7	17.3	40.3	23.8	40.3	275	325	good	38.3	pH 3.5; ammoniated during granulation.
01-09-3	12-57-0	19.6	18.0	42.2	20.0	42.2	250	425	good	43.0	pH 4.5; NH_4OH added.
01-09-3	12-57-0	21.8	20.0	47.1	11.1	47.1	250	425	good	45.8	Tried to increase yield.
01-10-3	12-57-0	19.6	18.0	42.2	20.0	42.2	350	425	--	--	Balanced the recycle product.
01-19-3	12-57-0	12.3	11.3	26.5	49.9	26.5	290	450	--	37.9	Insufficient wetting of solids.
02-06-3	12-57-0	12.3	11.3	26.5	50.0	26.5	225	425	v. poor	30.3	Granules angular.
02-07-3	12-57-0	12.3	11.3	26.5	50.0	26.5	275	450	v. poor	--	--

Table 7. HYGROSCOPICITY
(Weight gained, based on dry weight, %)

Fertilizer grade (Sample number)	Days in chamber			
	1	2	3	6
35% RH, 30°C (86°F)				
14-24-8 (12-21-73)	1.8	1.6	1.7	1.7
12-24-12 Olin sample	1.3	1.1	1.1	1.2
12-24-12 (1-3-73)	2.9	2.8	2.7	2.8
12-24-12 (1-5-73)	2.6	2.7	2.8	2.8
16-31-0 (1-3-73)	1.1	1.0	1.0	1.2
14-14-14 (12-19-73)	2.9	2.6	2.7	2.7
12-12-12 Olin sample	0.7	0.5	0.6	0.6
12-24-12 (12-28-73)	0.7	0.5	0.6	0.7
40% RH, 30°C (86°F)				
14-24-8 (12-21-73)	5.3	5.7	6.5	8.7
14-14-14 (12-21-73)	4.0	4.6	4.4	5.5
12-24-12 (12-28-73)	4.8	5.5	5.9	7.0
12-24-12 (1-3-73)	0.9	1.6	2.4	3.9

Table 7 (continued). HYGROSCOPICITY
(Weight gained, based on dry weight, %)

Fertilizer grade (Sample number)	Days in chamber			
	1	2	3	6
40% RH, 30°C (86°F)				
12-24-12 (1-5-73)	4.9	4.9	5.4	6.0
16-31-0 (1-3-73)	4.3	4.8	4.7	4.5
12-12-12 Olin sample	1.8	1.3	1.2	1.2
12-24-12 Olin sample	1.7	1.4	1.6	1.4

Table 8. CRITICAL RELATIVE HUMIDITY AT 30°C (86°F)

Fertilizer grades (Sample number)	Critical relative Humidity, %	Sample size, gm
14-24-8 (12-20-73)	26.9	1.1
14-14-14 (12-19-73)	65.1	1.2
12-24-12 (12-28-73)	32.5	1.0
16-31-0 (1-3-73)	29.4	1.2
12-12-12 Olin sample	79.1	1.1
12-24-12 Olin sample	32.6	1.1

Table 9. RELATIVE RATES OF SOLUTION

(Sample dissolved in 10 minutes, %)

Grade Sample	Solution Rate				Total Solids, %
	N	Total P_2O_5	K	pH	
14-14-14 12-15-72	3.0	4.2	2.5	2.5	21.6
12-12-12 Olin Sample	2.4	5.2	1.2	3.5	14.5
12-24-12 12-29-72	3.0	6.5	2.0	3.1	21.9
14-14-08 12-21-72	2.8	5.4	1.5	2.5	20.3
12-24-12 Olin Sample	2.3	3.5	1.4	3.5	15.2
12-24-12 12-29-72	0.0	1.1	0.5	3.5	--

Rate of moisture pick-up - Table 10 presents comparative data for several fertilizer grades and two product sources. The Olin products again show somewhat less sensitivity to moisture in storage. However, the acceptable limits should be defined differently for the Ferguson and the Olin products in view of the observed favorable warehouse storage of the Ferguson product for more than one year.

Conclusions

The results obtained in the laboratory investigation were used to select flow sheets and equipment for the pilot plant phase. The data defined many parametric windows within which a good quality fertilizer could be produced. These tests also eliminated much preliminary work towards defining the operating parameters needed to produce the various grades of fertilizer desired.

Table 10. RATE OF HYDROLYSIS

Fertilizer Grade Sample number	Week in Chamber 82%, RH	Moisture,%	Total P_2O_5, %	P as PP % of Total	N, %	K_2O, %	pH
14-14-14	-	1.7	20.8	31.7	13.1	12.6	2.7
12-15-72	1	9.2	19.4	24.2	-	-	-
	2	19.7	19.9	28.6	14.1	19.3	2.5
	3	29.7	20.2	37.4	13.5	13.1	2.6
12-12-12	-	1.6	14.6	1.2	11.5	12.6	3.4
Olin	1	5.2	14.3	1.3	11.1	11.7	3.5
	2	5.2	14.3	13.2	11.7	-	3.8
	3	16.8	11.5	7.8	12.1	12.6	3.9
14-24-8	-	1.7	30.5	25.0	13.0	6.3	2.6
	1	16.2	29.4	19.6	-	-	-
	2	23.3	29.5	0	13.4	6.8	2.3
	3	25.7	28.8	14.8	13.4	-	2.5
16-31-0	-	0.6	29.6	20.1	14.8	0.1	2.8
12-28-72	1	9.4	30.1	14.3	14.9	0	2.5
	2	20.2	32.2	15.9	15.0	-	2.5
	3	21.3	32.1	14.2	15.3	-	2.6
12-24-12	-	0.4	30.5	41.5	11.8	10.5	3.3
12-28-72	1	11.1	29.6	36,4	12.6	11.8	3.0
	2	22.8	29.8	38.6	12.3	-	3.1
	3	29.8	32.3	44.0	12.5	11.5	3.1
12-24-12	-	1.0	24.4	0.6	12.2	11.6	3.4
Olin	1	7.1	24.1	0.5	12.1	11.5	3.4
	2	11.8	24.6	7.4	12.4	-	3.6
	3	20.3	25.7	3.6	12.5	11.5	3.5

SECTION V

PILOT PLANTS

INTRODUCTION

Two pilot plants were constructed and operated. One had a capacity of 45 kg/hr (100 lbs/hr) and the other, a capacity of 454 kg/hr (1000 lbs/hr). The information obtained on operating parameters and equipment behavior in the small unit was applied to the design of the larger plant. Equipment design and operating data obtained during pilot operations were used to formulate the design of the scale-up commercial plants described in Section VI.

DESIGNS

Of the many preliminary designs considered, three were chosen for detailed consideration: Alternates I, II and III. Material and energy balances were developed for these alternates based upon the laboratory optimization study results. It became apparent that Alternate I, with its higher equipment and energy requirements, would not be as desirable as Alternate II or III. Therefore, Alternate I was not investigated beyond the computation state.

Alternates II and III were quite similar. Therefore, only minor changes of pilot plant equipment were needed to test both designs.

Alternate I flow sheet and equipment are presented in the Appendix, Section IX. Energy balances for all alternates are also included in the Appendix. Only Alternates II and III are discussed in this section.

The flow sheets for Alternates II and III are shown in Figure 3. To prevent excessive duplication of figures to be presented, Figure 3 also includes data developed for the 227 Mt/d scale-up which is discussed in the next section. The basic process concepts and equipment are described below. The results and conclusions of the pilot plant operations are presented separately for each plant size.

STREAM Nº.	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩	⑪	⑫	⑬	⑭	⑮	⑯	⑰	⑱	⑲
DESCRIPTION	H_3PO_4	NH_3	STM.	MELT	RECYCLE	FILL *	KCL	AS	MIX	PROD	PROD MIX	MIX	+5	PROD	PROD	-14	PROD	H_2O VAP.	NH_3
FLOWITPHIMETRIC	2.8	0.5	0.84	2.61	17.1	41%	2.4	4.93	7.74	20.51	28.25	30.12	2.04	10.11	10.11	7.94	10.11	0.69	VARIES
TEMP °C	21.1	21.1	100	130±	82	21%	21.1	21.1	21.1	110	110	110	100	100	100	100	55	60	21.1

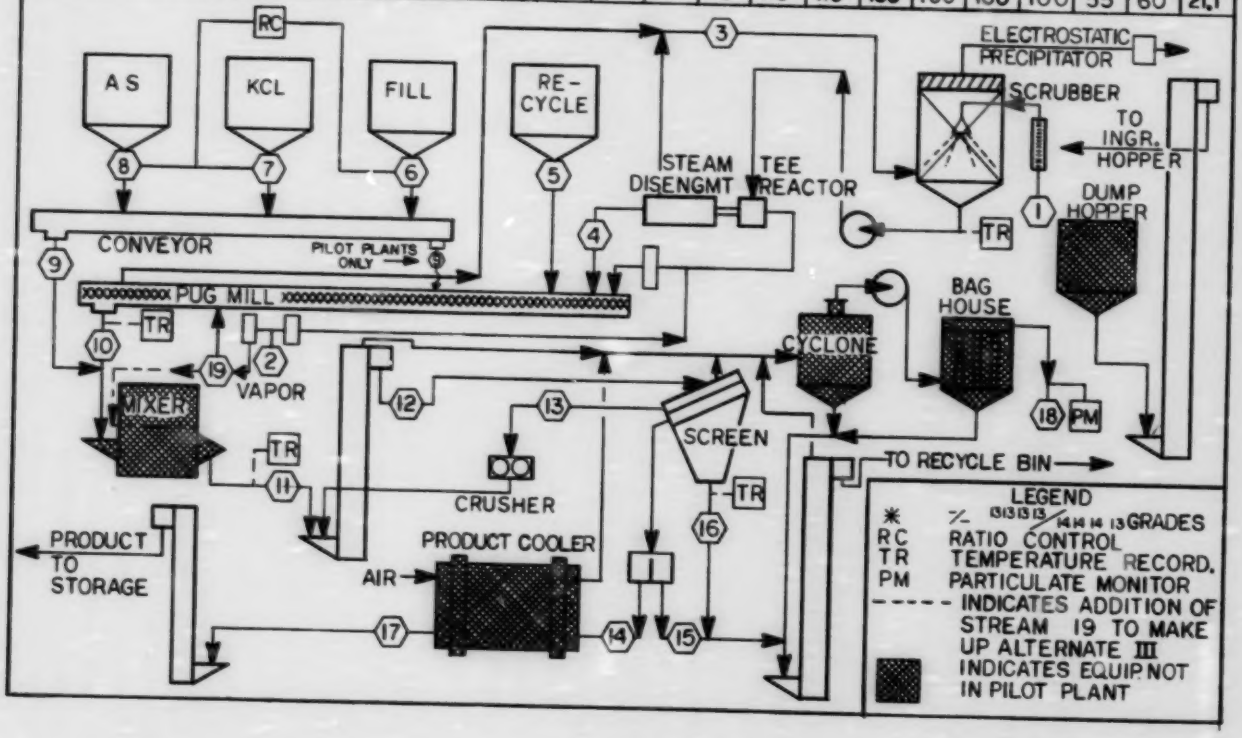


Figure 3. Alternate II and III flow sheet for 227 Mt/d (250 st/d) pilot plant producing grade 13-13-13-13.

ALTERNATE II

Basic process and equipment were:

Ammonium Polyphosphate Melt Production - Phosphoric acid was mixed with ammonia in a tee reactor chamber to produce ammonium phosphate and ammonium polyphosphate. A drawing of this is shown in Figure 4. An acid scrubber in the phosphoric acid feedline captured ammonia lost from the steam disengagement chamber which separated water vapor and ammonia from the melt, plus that in the pug mill vent.

Mixing the Melt with Solid Material - A pug mill was chosen as the granulation mill. This was done because laboratory experiments had shown that vigorous pugging is required to mix the viscous ammonium polyphosphate melt with the dry ammonium sulfate, potassium chloride, recycle solids and other materials. Two pug mill designs for the pilot plant are shown in Figure 5. Preheating of the solids was required for the dry materials stream. This preheating enabled the melt to be mixed with the solids before crystallization occurred. In the small pilot plant, the solids were heated as they were fed from the bins. The sensible heat of the hot product was wasted. In the large pilot plant, and in the 227 Mt/d scale-up plant, the raw materials were added to the product from the pug mill in order to utilize the product heat and to control crystallization.

Sizing, Recycle, and Storage Steps - Material from the granulation process was screened. Oversize material was sent to the crusher and was resieved. Fine material, which in the large pilot plant and in the 227 Mt/d flow chart contained heated raw solids, was recycled. The intermediate, market size was cooled and sent to storage.

Pollution Control - The steam and ammonia separated in the steam disengagement chamber was scrubbed by incoming phosphoric acid in the ammonium scrubbing unit. Pug mill vapors and particulate matter were also piped to this scrubber. Effluent vapors from the scrubber which contain ammonium chloride were removed and sent to an electrostatic precipitator. The gaseous effluent from the precipitator was vented to the atmosphere. The solids collected from the scrubbing operation and the precipitator were recycled. Table 11 presents representative data for this operation.

In the pilot plants, no effort was made to control dust from the dry handling equipment. In the scale-up plants, this material was cleaned by cyclones and bag filters and was recycled.

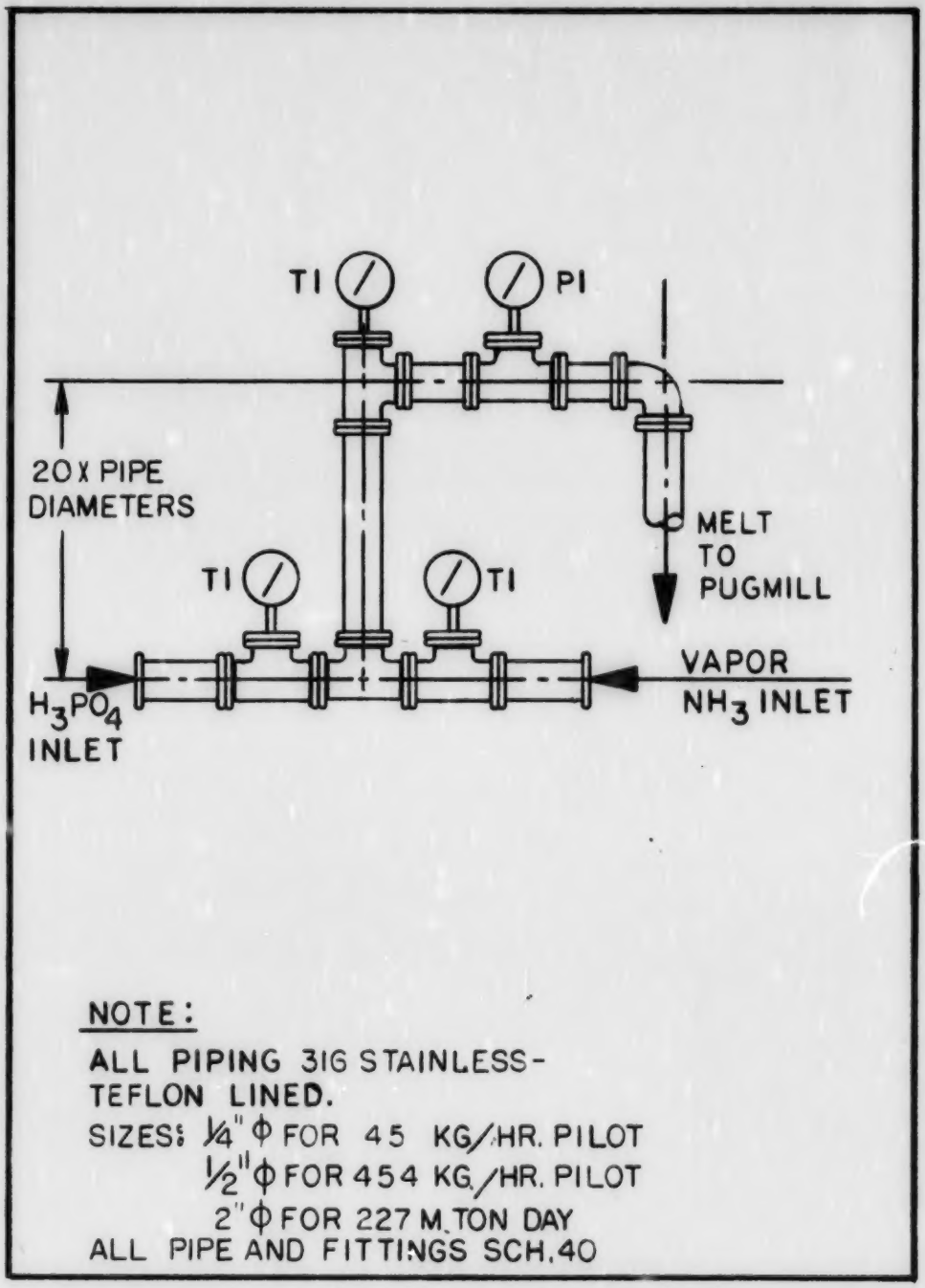


Figure 4. Tee reactor design.

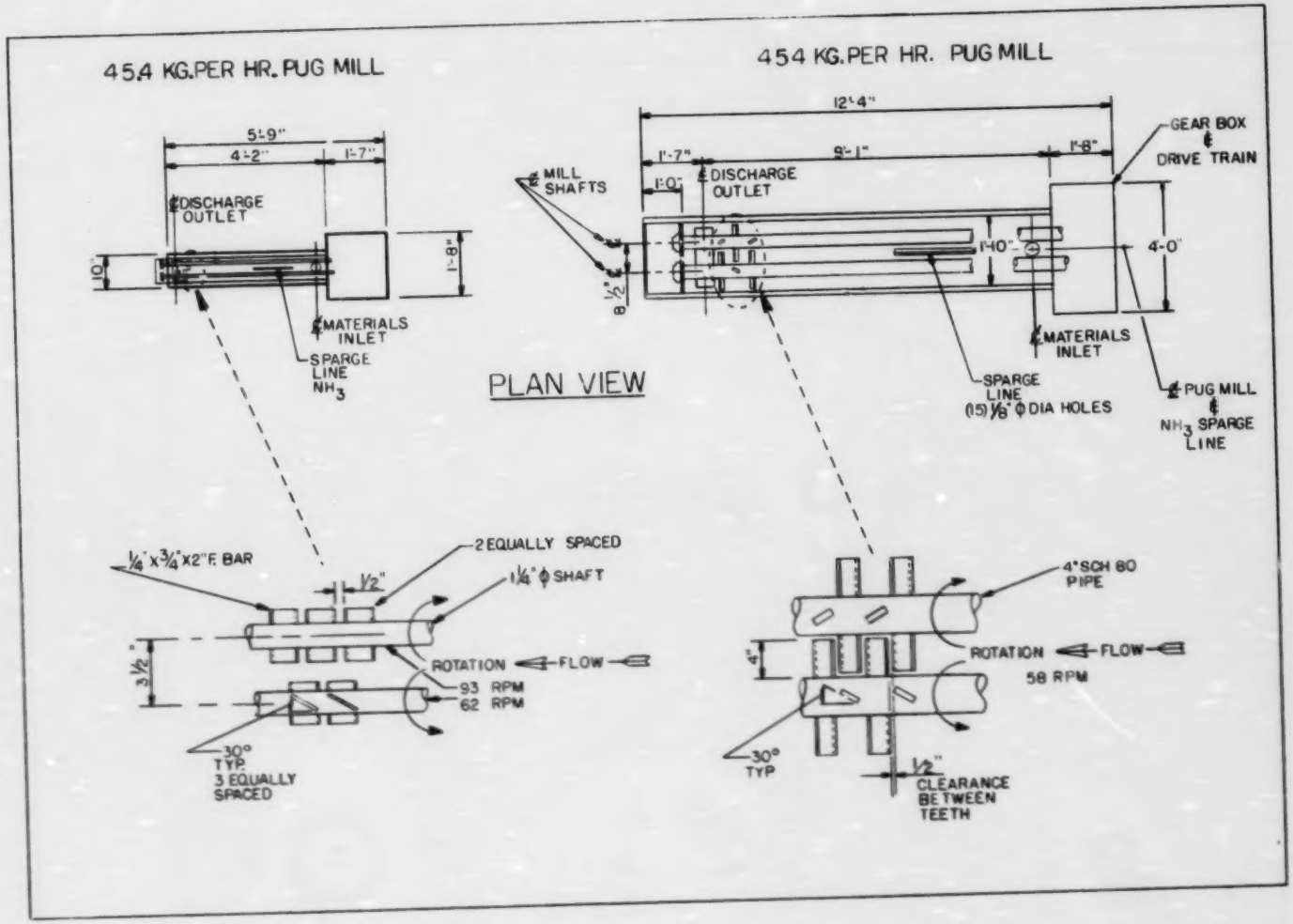


Figure 5. Pug mill designs for pilot plants.

Table 11. CHEMICAL ANALYSIS OF PUG MILL EXHAUST
(Percent total stream)

Sample	A	B	C	D	E
NH_3 - N	6.84[a]	2.13[a]	1.02[b]	0.71[b]	0.82[b,c]
Sulfate	0.01	0.01	0.01	0.01	0.01
Chloride	0.23	0.55	0.41	0.68	0.04
P_2O_5	0.01	0.01	0.01	0.01	0.01
H_2O	93.27	97.30	98.55	98.59	99.01

[a]Excess ammonia added in pug mill.

[b]Sample D before, and Sample E after, a Gothard "Fulgor" multistage electrostatic precipitator.

[c]Equivalent to 10 milligrams per cubic meter (mg/m).

Notes:

Solids collected off first stage plates: Nitrogen 15.00% Sulfate 15.40%, P_2O_5 27.80%, Potash 7.44%, Chloride 9.02%, Ammonium Chloride 3.40%.

Accuracy limits of analytical methods - 0.01%.

ALTERNATE III

Basic processes and equipment were:

Ammonium Polyphosphate Melt Production - The process was the same as in Alternate II, except that some ammonia was diverted to the downstream end of the pug mill. This produced a more acidic melt with desirable wetting and viscosity properties.

Mixing the Melt with Solid Materials - The process was the same as in Alternate II, except that diverted ammonia was sparged into the lower end of the pug mill. In the cases of the prototype and commercial plants, part of the diverted ammonia was sparged into a separate mixing drum to insure attainment of a one-to-one ratio of ammonia to phosphoric acid and to insure non-hydroscopic product quality.

Sizing, Recycle and Storage - Same as in Alternate II.

Pollution Control - Same as in Alternate II.

OPERATION OF THE 45 kg/hr PILOT PLANT

Upon completion of construction of the Alternate II design plant, an operational checkout was conducted to determine the effectiveness of mechanical configurations and equipment sizing in producing fertilizer grades 13-13-13-13 and 12-24-12-13. Work was concentrated on these two grades because they represent two segments of a spectrum of granular materials which can be made by the methods proposed in this report. Grade 12-24-12-13, which has a solids-to-melt ratio slightly less than 2, was easy to handle and to form into a marketable product. Grade 13-13-13-13, which has a solids to melt ratio of slightly higher than 3, was difficult to process. However, grade 13-13-13-13 was the most desirable since increasing its use would increase the amount of ammonium sulfate waste product that could be utilized. Test results are presented in Table A-3 of the Appendix. This table also includes pertinent physical and chemical conclusions from each run. In the pilot plant and the laboratory work, the chemical content of the product was relatively closely fixed by the nature of the raw materials and recycle. Indeed, at steady state operation, the chemical content of the recycled material did not affect the output stream. In the pilot plants, as in the laboratory, it was the granular quality which was the dependent variable and was controlled by the acid-to-ammonia ratio in the tee reactor, reaction temperature, pug mill temperature and the ratio of recycled material to product.

Pug mills, of necessity, are ruggedly built. The shafts must be non-deflecting, as they transmit relatively large amounts of horsepower. As a result, small pug mills are built with close clearance and have relatively small flow areas. For example, as shown in Figure 5, the smaller pug mill had a 1-1/4 inch shaft and 3/4 inch blades; the larger mill had a 4 inch shaft, 4 inch blades and a correspondingly larger flow area. This relationship is even more pronounced in a commercial mill, in which the blade length may be two or three times the shaft diameter.

The purpose of using a pug mill was to cause intimate mixing of the melt and solids to promote crystallization, or granulation. Ideally, this phenomenon would occur within the mixture that was being processed as it was cooled and mixed. However, the mechanical equipment constituted a heat transfer surface which also affected the granulation process. When the equipment surface temperature was above the temperature of the mixture being processed, excessive fluidity tended to occur. In such instances, when crystallization finally was achieved, there was a tendency for the mixture to form large lumps rather than granules. These lumps adhered to the mechanism and tended to plug it, thus effectively destroying the mixing action. Alternatively, when the equipment surface was below the mixture temperature, the melt tended to crystallize on the equipment surface, again resulting in plugging of the equipment. For this reason, the performance of the pilot plant pug mill was not completely indicative of the performance of large scale pug mills. This factor was taken into consideration in the test evaluations.

It very soon became apparent that Alternate II produced a melt too viscous to wet the solids in the pilot plant pug mill, and good granulation could not be obtained. The plant configuration was changed to Alternate III, which entails the two step generation of a melt. In the first step, part of the ammonia and all of the phosphoric acid were mixed in a tee reactor. This mixture produced an acidic, low viscosity melt. This melt was piped to a pug mill where it was mixed with solids. Thereafter, ammoniation was completed.

From the test data, it was concluded that optimum material and operating parameters for product grades 13-13-13-13 and 12-24-12-13 are in the ranges presented in Table 12.

OPERATION OF 454 kg/hr PLANT

Reconfiguration of the 45 kg/hr plant into the 454 kg/hr plant for design Alternate III was based upon the results obtained from operation of the 45 kg/hr plant. Prior experience with smaller unit configuration enabled the start-up of the 454 kg/hr unit to be accomplished with a minimum of trouble. Only minor adjustments were required.

Table 12. OPTIMUM OPERATING PARAMETERS FOR THE 45.6 kg/hr (100 lb/hr) AND 454 kg/hr (1000 lb/hr)[a] PILOT PLANTS

(13-13-13-13 Grade)

Materials	kg/hr	lb/hr
Phosphoric acid 52% P_2O_5	10.5	23.7
Ammonia	1.6	3.5
Potash	9.7	21.1
Ammonium sulfate	22.1	48.5
Filler	31.3	69.0
Recycle-variable up to	13.6	30.0

(12-24-12-12 Grade)

Materials	kg/hr	lb/hr
Phosphoric acid 52% P_2O_5	38.2	84.2
Ammonia	5.7	12.5
Potash	18.1	40.0
Ammonium sulfate	29.7	65.4
Filler	2.4	5.3
Recycle-variable up to	75.0	165.0

[a]for 454 kg/hr plant, multiply all values above by 10.

OPTIMUM OPERATING PARAMETERS FOR BOTH GRADES

Tee reactor temperature	110-130° C
Recycle temperature	82° C
Ammonium sulfate and potassium chloride particle sizes	60% (-20 + 100)
Recycle/product ratio	
13-13-13-13	0.3/1.0
12-24-12-13	0.8/1.0

Operation of the 454 kg/hr pilot plant proceeded rapidly due to previous identification of the significant operating parameters. Some of the operational problems encountered with the 45 kg/hr plant, primarily mixing effectiveness and temperature control, were eliminated in the 454 kg/hr pilot plant. The larger unit size smoothed out some of the fluctuations encountered in the 45 kg/hr plant. Because of some difficulty with output sizing from the previously used crusher, a chain mill was installed to reduce oversized products in this plant.

Product grades 13-13-13-13 and 12-24-12-13 were produced in this test operation. From these results, optimum material and operating parameters were found to be essentially the same as for the 45 kg/hr plant. The optimum parameter ranges presented in Table 12 apply to the 454 kg/hr plant also.

To test the durability of the equipment and process, a five day continuous run was made producing 454 kg/hr of mixed fertilizer. Grades 13-13-13-13, 12-23-12-13 and 18-18-0-0 were produced with satisfactory granulation. Data and comments on each sample are presented in Table 13. Results show this process can be varied to produce several grades, and the production is stable.

GENERAL PROCESS AND OPERATION CONCLUSIONS

The following comments and observations made during the laboratory and pilot plant studies are relevant to this fertilizer production process.

1. The process depends upon the melt to agglomerate the solids. Therefore, the solid-to-melt ratio and the properties of the melt, i.e. its viscosity and wetting ability, affect granulation.

2. It is apparent that in steady state operation a change in the recycle rate will have no affect on the chemical composition of the product. However, changing this ratio will result in a significant change of the solids-to-melt ratio in the mixing zone.

3. The ability of the melt to coat and bind the particles is affected by changes in the raw material, in the recycle fines and in the relative surface per unit volume of the dry ingredients.

Table 13. DATA FROM FIVE DAY RUN IN 454 kg/hr (100 lb/hr) PLANT

Sample Number	Chemical Analysis %						Comments
	M	P	PP	K	H_2O	pH	
Grade 13-13-13-13							
Nov. 21-1	13.2	11.2	2.7	15.8	0.6	3.4	121°C (250°F) in reactor. Granulation fair but useable.
2	13.0	11.1	6.6	16.9	0.7	2.9	Tee Reactor problem, granulation fair and somewhat steady.
3	13.1	11.9	3.7	16.1	0.7	3.1	Granulation fair, Pug Mill got too wet and caused some problems.
4	13.1	12.1	4.9	15.7	0.6	3.5	Fair granulation, stable.
Nov. 22-1	13.7	11.8	5.0	15.1	0.5	3.5	Fair granulation, but variable, too much recycle.
Grade 18-18-0-13							
Nov. 22-2	18.1	12.4	4.8	0.99	0.3	3.7	Granulation questionable, Reactor 143°C (250°F)
3	18.5	12.1	4.7	-	0.2	3.5	Good granulation-stable
4	18.7	13.0	5.7	-	0.7	4.3	Good granulation, acid pump problems, resumed good granulation and stable.
Nov. 23-1	18.1	12.7	4.3	-	0.4	4.9	Reactor Temp. 106°C (250°F) good granulation. Pug Mill wet at one time. Very good granulation.
Grade 12-24-12-13							
Nov. 23-1	12.8	20.6	7.2	13.8	0.8	3.7	Fair granulation, Exhaust fan trouble, very good granulation after repair
Nov. 24-1	12.4	20.3	9.6	12.9	0.4	3.7	Repair Pug Mill transmission poor to good granulation.
2	14.0	22.1	6.1	9.1	0.5	7.1	Stable and good granulation. Reactor Temp. 99°C (210°F)

Table 13. (Continued) DATA FROM FIVE DAY RUN IN 454 kg/hr (100 lb/hr) PLANT

Sample Number	Chemical Analysis %						Comments
	M	P	PP	K	H_2O	pH	
3	13.0	22.7	4.6	11.3	0.5	3.6	Reactor 99°C (210°F) good and stable granulation.
Nov. 25-1	13.5	20.6	2.9	11.1	0.7	3.7	Pug Mill very sensitive to over agglomeration.
Grade 13-13-13-13							
2	13.8	12.7	8.2	14.3	0.9	4.2	Granulation varied, usually good.
3	14.8	12.0	11.3	13.1	0.4	4.8	Granulation fair to good periods of Pug Mill wetness. Tee Reactor 99°C (210°F).
Grade 12-24-12-13							
4	12.2	18.7	9.6	16.7	0.7	4.8	Tee Reactor 110°C (230°F) good granulation. Acid line plugged which caused some problems.

4. As the grade formulation is fixed by the composition of the raw materials which are to be used, each grade has a fixed raw material solids-to-melt ratio. However, the total solids-to-melt ratio will vary, depending upon the amount of fines which are recycled. Two illustrations of the increase of solids-to-melt ratio with fines recycle are shown below for the grades that were investigated.

Grade	Raw Material Solids-to-Melt With No Recycle	Total Solids-to-Melt Ratio With 300 Parts of Fines Recycled per 1000 Parts of Product
13-13-13-13	3.1 to 1	4.2 to 1
12-24-12-13	1.9 to 1	2.8 to 1

5. It is important that solids and melt initially are mixed at temperatures above the melt crystallization point to attain satisfactory wetting and agglomeration. Normally, this would be accomplished by heating the raw materials. However, it was found that satisfactory mixing could be attained without supplemental heating by adding the unheated raw materials downstream of the point at which melt and recycle materials are mixed.

6. For high solids-to-melt ratios, it is very desirable to control the melt viscosity by diverting some of the ammonia from the reactor to the pug mill for final ammoniation near the end of the granulation step.

7. The larger pug mill which was used in the 454 kg/hr pilot plant, with its greater free volume, proved much more effective and exhibited a greater granulation efficiency, i.e. produced a greater yield of market size granules per pass, than did smaller pug mills which were used in the 45 kg/hr pilot plant.

POLLUTION CONTROL CONSIDERATIONS

A major objective of this project was to utilize process steps which avoid or minimize polluting effluents. This will reduce adverse impacts of future fertilizer plants on the environment and, possibly, will provide a means whereby existing plants may be converted to reduce pollution as an alternative to the installation of expensive pollution control devices. The following discussion identifies the pollution characteristics of conventional and melt process fertilizer production.

In the typical ammonium phosphate sulfate plant, concentrated sulfuric acid, "filter strength" phosphoric acid and ammonia are combined in the tank preneutralizer to produce a slurry. Solubility properties require the operator to maintain relatively low pH and high temperature. Vapors from these conditions tend to have a high fluoride concentration. The partially ammoniated slurry flows to the ammoniator granulator where it is combined with more ammonia, potash, filler and recycle. Fumes of ammonium chloride and ammonium fluoride escape from this process and are sent to an acid scrubber. A conflict involved in the scrubber operation is that when pH levels are above 5.3, non-scrubbable ammonium fluoride aerosols form and ammonia losses occur; when pH levels are below 2.0 fluoride losses occur. Therefore, pH levels must be carefully maintained between these limits.

Although approximately the same total amounts of fluorine must be treated regardless of the process, it is much more efficient and economical to treat the fumes from acid production at a large, central facility than to scrub process off-gases at a number of regional granulation plants.

Thus, the advantages of the melt process are:

1. No free sulfuric acid is used, therefore reducing the heat, steam and fluorine involved.

2. The melt process uses high concentration phosphoric acid rather than "filter strength" in order to produce minimum water and fluoride emissions.

3. The tee reactor, with a higher nitrogen-to-phosphate ratio, retains fluorine in the melt.

4. Low water evolution produces less fluorine loss. (To monitor the potential fluorine problem in the melt process, a number of measurements was made of the fluorine-to-P_2O_5 ratios in the feed and in the product. There was no detectable change in

these ratios, indicating a minimum problem from this process as compared to the conventional production method.)

5. The melt process requires a smaller addition of ammonia to the granulator. Therefore, the volume of gaseous effluent which must be handled and treated is reduced.

6. Only a small quantity of ammonium chloride aerosol is generated.

SECTION VI

SCALE-UP PROTOTYPE AND FULL SIZE PLANT

OBJECTIVES

The objectives of this section were to prepare detailed design and cost figures for the best technical manufacturing process plants to produce 227 Mt/d and 907 Mt/d of the common grades of fertilizer from the raw materials previously discussed. The plants were to utilize a melt technique and were to be based upon the laboratory and pilot plant studies of the previous sections. Adequate pollution controls were to be included.

The 227 Mt/d size is recommended for a prototype plant because it has been most commonly used in regional granulation facilities. The 907 Mt/d size is suggested for large commercial installations in which most of the economies of scale can be realized.

BASIC DESIGN CONSIDERATIONS

In order to be sure that the proposed plant would be commercially and technically sound and comparable with a plant based on current aqueous methods, additional consideration was given to the three factors listed below before the final plant design was established.

1. Did the market analysis indicate that the design N-P-K-S fertilizer product was being used in significant quantities?

2. Would the plant design incorporate enough flexibility to permit production of fertilizer grades other than that for which the plant had been designed?

3. Did the laboratory study indicate that a critical N-P-K-S grade had been selected as the basis for the plant design?

Based on these considerations, an N-P-K-S ratio of 1-1-1-1 was chosen for the study. The market analysis showed that a 1-1-1 ratio, or very near a 1-1-1 ratio, accounted for approximately 11 to 12% of the total mixed fertilizer market. The laboratory study had shown that a 1-1-1 ratio was the most difficult to produce. This ratio has the lowest concentration of ammonium phosphate - polyphosphate melt. Therefore, it is most difficult for the melt to satisfactorily wet the dry raw products to produce good granulation. From the various process flow sheets considered, it was concluded that the plant could produce the other significant grades shown in the market analysis if the plant had the process steps necessary to produce a 1-1-1-1 ratio N-P-K-S fertilizer.

PROTOTYPE 227 Mt/d PLANT

The plant design was based on Alternate III because it has lower capital and operating requirements than the other two Alternates. Details of capital and operating requirements are discussed later in this section.

An isometric drawing of the proposed plant is shown in Figure 6.

Equipment Design

Details of the major plant components are given in Table 14.

Comments pertaining to the most significant equipment and its operation are detailed below.

1. Tee Reactor - The phosphoric acid and ammonia are mixed and reacted to produce the ammonium phosphate - polyphosphate melt. Temperature control of the melt is important in producing optimum mixing with solid recycled material in the pug mill. Tee reactor details are shown in Figure 4. Separation of water from the melt is necessary to produce good melt and good granulation. The steam disengagement chamber, an integral part of the tee reactor, also separates excess ammonia vapor from the melt. The ammonia vapor is returned to the acid scrubber.

2. Pug Mill - This equipment is used to mix the recycled product fines and the melt. Granulation occurs following mixing. The temperature of the pug mill is important for proper granulation of the product. When the temperature of the incoming

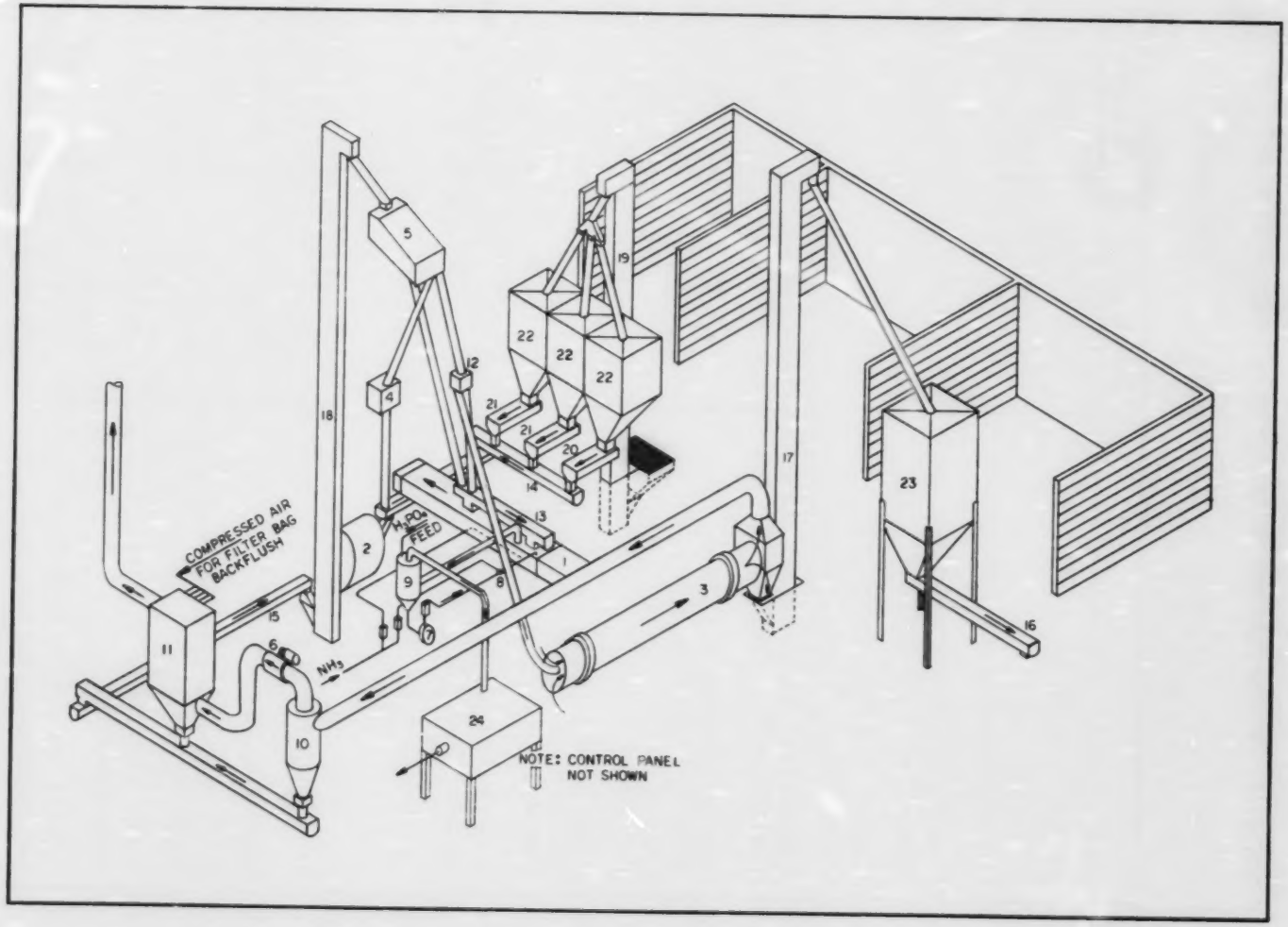


Figure 6. Isometric drawing of 227 Mt/d (250 st/d) plant - Alternate III.

Table 14. MAJOR COMPONENTS OF 227 Mt/d (250 st/d) PLANT

Item		Motor Size, (HP)	Quantity
1.	0.91m x 9.4m (36 in x 30 ft) Pug Mill	150	1
2	4.54 ton (5 ton) Rotary Drum Mixer	25	1
3.	1.8m dia. x 12m (6 ft. x 40 ft OAL) Rotary Drum Prod. Cooler	25	1
4.	1.2m x 1.5m (48 in x 60 in) Chain Mill	30	1
5.	3.7m x 1.8m (12 ft x 6 ft) Deck 3 Deck totally enclosed vi. screen	20	1
6.	17,000 CFM Blower @ 15.24cm (6 in) H_2O Pressure	25	1
7.	37.9 l/min. (10 GPM) Acid Pump	3	1
8.	5.0cm (2 in) Teflon lined Tee Reactor, and Steam Disengagement Chamber.	-	1
9.	0.7m dia. x 1.8m (30 in x 6 ft) Cascade Steam - NH_3 Vapor Scrubber	-	1
10.	1.2m dia. x 3.1m (4 ft dia. x 10 ft OAL) Dust Cyclone	-	1
11.	#130 S-8-20 Micro-Pulsaire Bag Filter 113.8 square m. (1225 sq ft)	-	1
12.	Recycle Splitter Valve	1	1
13.	0.3 x 3.66m (12 in x 12 ft) Screw Conveyor	5	1
14.	0.23 x 6.2m (9 in x 20 ft) Screw Conveyor	3	2
15.	0.3 x 7.32m (12 in x 24 ft) Screw Conveyor	5	2

Table 14. (Continued) MAJOR COMPONENTS OF 227 Mt/d (250 st/d) PLANT

Item		Motor Size, (HP)	Quantity
16.	0.36 x 7.32 (14 in x 24 ft) Product Loadout Screw Conveyor	10	1
17.	27.2 Mt/hr (30 st/hr) Elevator 22.9m (75 ft) Lift	10	1
18.	45.4 Mt/hr (50 st/hr) Bucket Elevator 24.4m (80 ft) Lift	15	1
19.	68.0 Mt/hr (75 st/hr) Bucket Elevator 18.3 (60 ft) Lift	15	1
20.	4.54 Mt/hr (5 st/hr) Weigh Belt	1	2
21.	9.08 Mt/hr (10 st/hr) Weigh Belt	1 1/2	1
22.	18.16 Mt (20 st) Ingredient Holding Bin	-	3
23.	52.2 Mt (60 st) Finished Product Surge Bin	-	1
24.	Electrostatic Precipitator	-	1
25.	Ratio Controller (Ammonia & Phosphoric Acid)	-	1
26.	Temperature Recorder - 1 Pen & Monitor	-	1
27.	Recorder - 3 pen	-	1
28.	Recorder - 4 Station Monitor	-	1

solids is not within a specified range, the result is poor granulation or no granulation. When cooling occurs too rapidly, melt crystallizes without mixing with solids.

3. Vibrating Screen Unit - This unit separates market size product (-5 to +14 mesh) from oversize product (+5 mesh) and from fines (-14 mesh). Improper separation will give either a lumpy or a dusty product.

4. Oversize Product Crusher - This takes the oversize materials separated in the vibrating screen unit and crushes them to a market size product. Careful operation is necessary to avoid a buildup of fines or of oversize material.

5. Mixing Chamber and Product Handling Equipment - In the pilot plant operation, raw materials were added to the latter part of the pug mill to conserve heat and to improve granulation. In the full size plant, this is done in a separate rotary mixer downstream of the pug mill.

6. Product Cooler - The hot, market size product is cooled to approximately 171° C (160° F) or lower before being transported to storage. Ambient air is used as the coolant. This air must be cleaned of particulate matter before being discharged to the atmosphere.

7. Pollution Control Equipment - Steam and ammonia separated by the steam disengagement chamber, as well as vapors from the pug mill and mixer, are scrubbed by phosphoric acid in the ammonia scrubbing unit. An electrostatic precipitator is used to remove particulate ammonium chloride from acid-scrubbed vapors. This effluent stream quality is discussed in Section V.

   Cleaning of the cooler air is performed in two stages. The first stage employs a cyclone to remove the larger solids. The second stage consists of a pulsed-air bag filter in which the tubes are periodically back-flushed with air.

By using the melt production process and the specified control devices, it is possible to practically eliminate granular fertilizer plant pollution. Solids collected from both cleaning operations are returned to the recycle bin.

8. Process Control and Monitoring Instrumentation - The process instrumentation consists mainly of temperature monitors, temperature controllers, solids feeder controllers and feed ratio controllers.

   The temperature in the tee reactor is monitored and recorded. It is important that this temperature be controlled carefully to insure optimum temperature of the melt being fed to the granulator. Temperature control is achieved by regulating the amount of ammonia which is added at the tee reactor. To insure the proper proportion of ammonia and phosphoric acid, the flows of these materials are ratio-controlled. The small amount of ammonia which is not sent to the reactor is added to the granulator.

   The raw material hoppers have built-in level monitoring devices. Monitoring of the weigh belts is done with a 3-pen recorder, one pen for each raw material: potassium chloride, ammonium sulfate and any other material, such as filler. Monitoring insures that the desired mixed fertilizer analysis is being produced.

   Temperature monitoring and alarming at key points in the process can indicate any operational problem before it can produce a significant quantity of off-specification product. The points to be monitored are the phosphoric acid downstream of the ammonia scrubber, the product from the pug mill, the product and raw material mixture from the rotary drum mixer, and the recycle material from the vibrating screen.

   Environmentally sensitive plant emissions include particulate matter, ammonia vapors and phosphoric acid vapors. Particulate matter from sieves, conveyors and the pug mill is trapped by the cyclone and bag filter. All vapors and aerosols

are passed through the acid scrubber and precipitator before being vented. Dust traps are monitored intermittently with portable equipment. Exhaust from the precipitator is monitored continuously by automatic instruments equipped with alarm points.

Material and Energy Balance

The flow of materials through various components of the 227 Mt/d plant is shown across the top of Figure 3. These figures indicate amounts of materials to be handled by each component or process flow stream, assuming twenty-two hours of operation per day. Optimum temperatures of materials at various points in the flow sheet also are shown in Figure 3.

The material balance is for a 13-13-13-13 grade fertilizer. When other grades are produced, phosphoric acid, ammonia, filler, potassium chloride and ammonium sulfate flow rates are changed. The total quantity flow of materials through the various process steps will vary because of the recycle. Provision has been made in the equipment selection to handle the maximum quantities which may be required.

The energy balance for the 227 Mt/d prototype plant is shown in Figure 7. No allowance has been made for heat losses. The heat requirement shown in the flow sheet for Alternate III is satisfied by the reaction of ammonia with phosphoric acid. By using the unique Alternate III process of mixing raw materials with the hot product after granulation, heat is transferred directly to the raw materials, as described in Section V. Thus, the Alternate III process uses no additional fuel to heat incoming raw materials. Thermal loss is minimized, and power requirements are reduced.

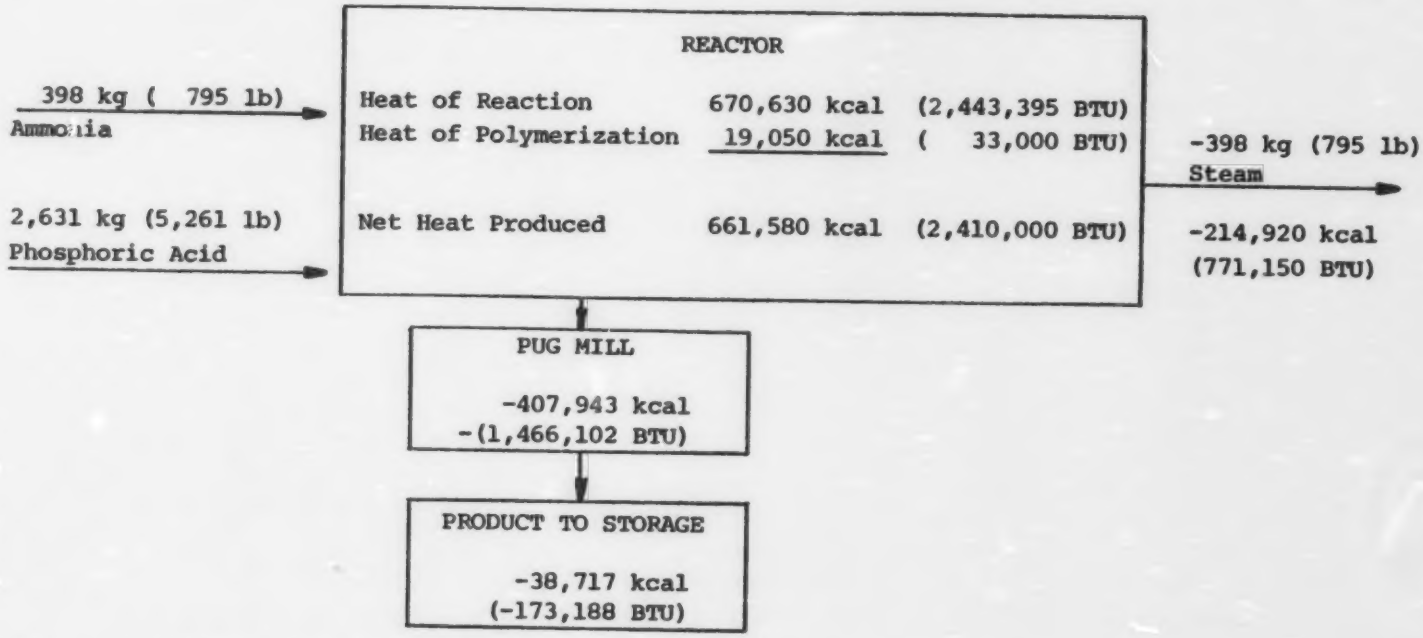
Investment Requirements and Manufacturing Costs

Analysis of the plant capital and manufacturing costs was completed. Details of this analysis are presented in Table 15. These cost estimates were prepared on the same basis as those for the commercial plant, as described below.

COMMERCIAL 907 Mt/d PLANT

Investment and manufacturing cost estimates were prepared for a new 907 Mt/d plant utilizing the technology described above, and for converting an existing 907 Mt/d aqueous process plant to this melt process.

Alternate III Producing a 13-13-13-13 Grade Fertilizer



Note: No allowance has been made for ambient heat loss.

Figure 7. Energy balance for a 227 Mt/d (250 st/d) prototype plant.

Table 15. 227 Mt/d (250 st/d) FERTILIZER PLANT COSTS USING ALTERNATE III FLOW SHEET FOR 13-13-13-13 GRADE FERTILIZER

Plant operates 330 d/yr to produce 74,828 Mt (82,500 st)

PLANT, EQUIPMENT, CONTROLS, BUILDINGS, ERECTION AND OFFSITES		
1. Equipment	$ 1,925,000	
2. Buildings	525,000	
Total Plant Investment	$ 2,450,000	
	Cost/Mt, $	**Cost/st, $**
MANUFACTURING COSTS		
1. Depreciation/t @ 6-2/3% per annum on plant cost $\frac{0.666 \times 2,450,000}{74,828}$ (.067) (2,450,000/82,500)	2.16	(1.96)
2. Raw Material Cost/t of 14-14-14-14	99.18	(90.00)
3. Direct Labor (0.46 man hr/t @ $4.00/hr)	3.05	(2.77)
4. Overhead (100% of direct labor)	3.05	(2.77)
5. Interest, 9% of 1/2 of plant costs	1.47	(1.34)
6. Interest in Inventory	3.01	(2.73)
7. Maintenance (20% of plant costs)	1.64	(1.49)
8. Supplies (20% of maintenance)	0.33	(.30)
9. Electricity, 50 kwh @ $.02/kwh	1.10	(1.00)
10. Analysis (20% of labor)	.61	(.55)
11. Insurance and Taxes (2% of plant cost)	.66	(.60)
12. Overformulation (2% of raw material costs)	1.98	(1.80)
13. 20% Return on Total Investment	13.23	(12.00)
Plant Cost $ 2,450,000 Inventory 2,500,000 (20% x Total $ 4,950,000/82,500 t)		
Total Cost	$ 131.47	($ 119.31)
14. Dealer Mark-Up (9% of total)	11.83	(10.74)
Selling Price	$ 143.30/Mt	($ 130.05/st)

As before, the estimates are based on the use of the Alternate III design to produce grade 13-13-13.

New Plant

The process flow sheet for Alternate I is shown in Figure A-2. The material balance assumes twenty-two hours of operation per day. The process flow sheet for Alternate II and III are shown in Figure 3 (flows x 4).

A comparison of capital and manufacturing costs for a new plant, as of June 1975, is shown in Table 15 for Alternates I and III. Alternate II is a less efficient minor modification of Alternate III; therefore, it is not included. The cost analysis clearly shows the advantage of using the Alternate III design. The total plant equipment investment is smaller; consequently, the cost per ton of fertilizer is lower.

Most of the services which form part of the overhead and utility costs of the plant were assumed to be a selected percentage of either plant capital or labor costs. These estimates were based upon many years of experience in fertilizer plant manufacturing. The assumptions made here are not to be considered absolute, but merely as a guide in comparing one process flow sheet with another and to assist in selecting the most economical, practical plant size and design.

Transportation costs to ship the fertilizer to the user were eliminated from the study by making both costs free on board the plant.

In order to compare one process flow sheet against the other, costs of transporting raw materials to the plant were considered equal and were included in the estimated prices of the raw materials. The prices of raw materials were based upon costs as of the date of this study. Ammonium sulfate was priced at $60.00/Mt, delivered, equivalent to the approximate market price of the contained ammonia. (It is recognized that this price may not be valid under present market conditions.) At this price, the manufacturer who produced ammonium sulfate as a by-product or in a waste stream would recover at least the cost of the ammonia used. For example, the cost of the ammonia used to scrub sulfur oxide radicals (SO_x) from the flue gases would be recovered from the sale of by-product ammonium sulfate produced.

CONVERTED PLANT

In order to determine the cost per ton of fertilizer in a 907 Mt/d plant which has been modified from present aqueous fertilizer technology, a five year old plant was used as a model. The plant cost approximately $3,200,000 five years ago. The price of the equipment

Table 16. NEW PLANT COST COMPARISON - ALTERNATES I AND III
PRODUCING 907 Mt/d (1000 st/d) OF 13-13-13-13 GRADE FERTILIZER

PLANT EQUIPMENT, CONTROLS, BUILDING, ERECTION AND OFFSETS

All equipment costs below include necessary structures, foundations, distribution equipment, downspouts and instrumentation.

Item	Description	Alternate I		Alternate III	
		Quan.	Total Price,$	Quan.	Total Price,$
1.	45 Mt/hr (50 st/hr) Bucket Elevators	2	56,000	1	28,000
2.	91 Mt/hr (100 st/hr) Bucket Elevators	2	98,000	2	98,000
3.	136 Mt/hr (150 st/hr) Bucket Elevators	-	-	1	42,000
4.	91 Mt/hr (100 st/hr) Pug Mill	1	140,000	1	140,000
5.	41 Mt/hr (45 st/hr) Product Cooler with Air System	1	280,000	1	280,000
6.	73 Mt/hr (80 st/hr) Preheater with Furnace	1	360,000	-	-
7.	91 Mt/hr (100 st/hr) Partial Cooler With Air System	1	360,000	-	-
8.	2,832 cu m/min (100,000 cu f/min) Dust Collector and Scrubber	1	840,000	-	-
9.	1,982 cu m/min (70,000 cu f/min) Dust Collector and Scrubber	-	-	1	270,000
10.	91 Mt/hr (100 st/hr) 3-Screen Tyler Hummer	1	140,000	-	-
11.	136 Mt/hr (150 st/hr) 3-Screen Tyler Hummer	-	-	1	210,000
12.	9 Mt/hr (10 st/hr) Chain Mill	1	70,000	1	70,000
13.	Miscellaneous Lot Screw Conveyors	1	112,000	1	112,000
14.	18 Mt Ing. (20 st Ing.) Bins with Vibrating Feeders	4	224,000	4	224,000
15.	Truck Dump Hopper Feeder	1	42,000	1	42,000
16.	Acid Scrubber	1	42,000	1	42,000
17.	Ammonium Polyphosphate Tee Reactor and Disengagement System	1	112,000	1	112,000

Table 16. (Continued) NEW PLANT COST COMPARISON - ALTERNATES I AND III
PRODUCING 907 Mt/d (1000 st/d) OF 13-13-13-13 GRADE FERTILIZER

Item	Description	Alternate I Quan.	Alternate I Total Price,$	Alternate III Quan.	Alternate III Total Price,$
18.	136 Mt/hr (150 st/hr) Rotary Mixer	-	-	1	280,000
19.	Electrostatic Precipitator	1	110,000	1	110,000
	Total Equipment Cost				
20.	Controls & Electrical System (20% of Equipt.)	-	600,000	-	412,000
21.	Erection of Equipment (30% of Equipment)	-	900,000	-	618,000
22.	Building 929 sq m (10,000 sq ft) @ $161.46/sq m	-	210,000	-	210,000
	Total Battery Limits, Items 1-22		4,696,000		3,300,000
23.	Offsite + 25% of Battery Limits	-	1,174,000		825,000
24.	90.718 Mt (100,000 st) of storage @ $16.53/t	-	2,100,000	-	2,100,000
	Total Battery Limits, Offsites and Storage		7,970,000		6,225,000

TOTAL MANUFACTURING COST		Alternate I Cost/Mt, $	Alternate I Cost/st, $	Alternate III Cost/Mt, $	Alternate III Cost/st, $
1.	Depreciation @ 6-2/3 % per annum of Plant Capital Investment, 0.067 x plant cost/299,310 Mt, or (330,000 st)	= 1.78	(1.62)	1.40	(1.26)
2.	Raw Material Cost	= 99.19	(90.00)	99.18	(90.00)
3.	Direct Labor	= 1.92	(1.74)	1.92	(1.74)
4.	Overhead = 100% of Direct Labor	= 1.92	(1.74)	1.92	(1.74)

Table 16. (Continued) NEW PLANT COST COMPARISON - ALTERNATES I AND III
PRODUCING 907 Mt/d (1000 st/d) OF 13-13-13-13 GRADE FERTILIZER

TOTAL MANUFACTURING COST		Alternate I		Alternate III	
		Cost/Mt, $	Cost/st, $	Cost/Mt, $	Cost/st, $
5. Interest = 9% of 1/2 Plant Cost 0.09 x plant cost/299,310 Mt, or (330,000 st)	=	1.20	(1.09)	.94	(.72)
6. Interest on Inventory	=	3.01	(2.73)	3.01	(2.73)
7. Maintenance = 5% of Plant Cost 0.05 x plant cost/299,310 Mt or (330,000 st)	=	1.33	(1.21)	.89	(.81)
8. Supplies = 20% of Maintenance	=	.26	(.24)	.18	(.16)
9. Electricity - 50 kwh @ $.01/kwh 5.1 kw @ $.005/kw	=	1.10	(1.00)	1.10	(1.00)
10. Water (1,460 gal @ $.20/1,000 gal)	=	.03	(.03)	--	--
11. Analysis 20% Labor	=	.38	(.35)	.38	(.35)
12. Insurance and Taxes = 2% of Plant Cost	=	.53	(.48)	.35	(.32)
13. Overformulation = 2% of Raw Material Cost	=	1.98	(1.80)	1.98	(1.80)
Sub Totals		114.62	(104.03)	113.49	(102.75)

14. 20% Return on Total Investment

	Alternate I	Alternate III				
Plant Costs	7,970,000	6,225,000				
Inventory	10,000,000	10,000,000				
Total	17,970,000	16,225,000				
Above total, per ton			=	12.08	(10.95)	10.84 (9.83)
15. Dealer Mark-Up = 9% of Total			=	11.40	(10.35)	11.19 (10.17)
Selling Price (per ton)				138.10	(125.33)	135.52 (122.75)

to modify the plant to produce fertilizer in accordance with the Alternate III design was added to the original cost. Depreciation was predicated on a useful life of ten years, the remaining estimated life of the original equipment. It was assumed that the added equipment would not be usable when the original equipment had reached the end of its useful life. This was considered to be a reasonable approach to depreciation and to be more conservative, i.e. to result in a higher depreciation cost, than any other approach which might be considered. Table 17 lists the estimated capital and manufacturing costs for producing grade 13-13-13-13 fertilizer in a modified 907 Mt/d plant.

CONCLUSIONS

At the start of this project, ammonium sulfate was a by-product or a waste product of several industries. It could be obtained at little or no cost and, indeed, presented a disposal problem. Calculations at that time indicated that the melt process had a favorable cost advantage over the conventional aqueous process for producing grade 13-13-13.

The fertilizer market recently has undergone a significant change. Most products, including ammonia, sulfuric acid and mixed fertilizer are in short supply and are very costly. Ammonium sulfate is extremely difficult to obtain, and its price fluctuates rapidly and erratically.

In an attempt to compare the cost of the fertilizer to be produced by ammonium sulfate, ammonium phosphate - polyphosphate melt and potassium chloride with the cost of other products, a price quotation was requested for 13-13-13 grade fertilizer. Listed below are the prices obtained.

PRODUCT	FERTILIZER	PRICE AT SHIPPING POINT
Agrico Chemical Co.	15-15-15	$178 per Short Ton[a] (Mississippi)
Agrico Chemical Co.	13-13-13	$148 per Short Ton[a] (Arkansas)

[a]Phone quote June 30, 1975. Dealer delivered bulk price.

The total cost of producing grade 13-13-13-13 was smaller than the prices indicated above, as demonstrated in Tables 15, 16 and 17. These evaluations are not altogether comparable, however. Currently, ammonium sulfate prices are so erratic that it is not possible to obtain a reasonable cost estimate. The melt process which has been developed has always been intended for use as a method of recovering and recycling chemicals with values that might otherwise be wasted.

Table 17. MODIFIED 907 Mt/d (1000 st/d) FERTILIZER PLANT COSTS PER ALTERNATE III FLOW SHEET FOR GRADE 13-13-13-13

An existing plant having an original cost of $3,200,000, five years old, is modified to the process flow sheet of Alternate III. The cost of fertilizer is then estimated based upon 10 years of plant depreciation rather than 15 years. This assumption is used since the improvements to the plant will be useful as long as the original parts are useful. This is considered to be the most reasonable, conservative approach.

Plant operates 330 days/year to produce 299,360 Mt (330,000 st)

PLANT EQUIPMENT, CONTROLS, BUILDING, ERECTION AND OFFSITES

The following equipment will be added to the original plant equipment:

1.	907 Mt/d (1000 st/d) Pug Mill	$ 158,000
2.	1982 cu m/min (70,000 cu f/min) Dust Collector and Scrubber	200,000
3.	Acid Scrubber	42,000
4.	Tee Reactor and Steam Disengagement Section	112,000
5.	NH_4Cl Electrostatic Precipitator	110,000
	Total Equipment Added	622,000
6.	Controls and Electrical Systems (16% of added plant equipment)	102,000
7.	Equipment Erection (25% of added plant equipment)	154,000
8.	Additional Building Requirements (48,000 f^2 @ $15/$f^2$)	72,000
	Total Modification Cost	950,000
	Original Plant Cost (5 years old)	3,200,000
	Total Original Plus Modification Cost	$ 4,150,000

Table 17. (Continued) MODIFIED 907 Mt/d (1000 st/d) FERTILIZER PLANT COSTS PER ALTERNATE III FLOW SHEET FOR GRADE 13-13-13-13

TOTAL MANUFACTURING COSTS		Cost/Mt, $	Cost/st, $
1. Depreciation per t @ 10% per annum on plant cost (0.10) (3,875,000)/299.310 Mt	=	1.39	(1.20)
2. Raw Materials costs/t	=	99.18	(90.00)
3. Direct Labor (0.32 man hr/Mt @ $6.62/hr)	=	1.92	
(0.29 man hr/st @ $6.62/hr)	=		(1.74)
4. Overhead (100% of Direct Labor)	=	1.92	(1.74)
5. Interest on Plant and Inventory, 9%	=	4.21	(3.82)
6. Maintenance (5% of plant costs) 0.05 x 3,875,000/299,310	=	.69	(.63)
8. Electricity, 50 kwh @ $.02/kwh	=	1.10	(1.00)
9. Analysis	=	.38	(.35)
10. Insurance and Taxes (2% of plant cost)	=	.28	(.23)
11. Overformulation (2% raw material cost)	=	1.98	(1.80)
12. 20% Return on Total Investment	=	9.47	(8.58)
Total Manufacturing Costs:		$ 122.66	($ 111.30)

Plant Costs: $ 4,150,000
Inventory: $ 10,000,000

As previously indicated, the costs of raw materials shown in Tables 15, 16 and 17 reflect the assumption that ammonium sulfate is priced at its ammonia value only, while recognizing that this price also is very high at the present time. If the cost of ammonium sulfate was to be included at any approximation of its current market price, then the cost of producing grade 13-13-13 by the melt process and the cost of its production by the aqueous process probably would be very close to the same amount.

The prices of many raw materials and of all mixed fertilizers behave in a manner which is very similar to that of commodities. Their prices are determined in large measure by the supply-demand relationship in the marketplace. It is quite likely that in the future the price of ammonium sulfate will fall much lower, and that waste and by-product ammonium sulfate will again be sold at the cost of their contained ammonia. Each metric ton of ammonium sulfate will contain $19.00 worth of sulfuric acid (at current market prices). This is equivalent to a savings of $10/Mt for grade 13-13-13 which can be realized when the melt process is employed.

As noted previously, the capital and energy charges for the melt process will be lower than for the aqueous process because the dryer and its ancillary equipment are not needed, pollution control requirements are less and the melt process operates with a lower recycle ratio.

The overall effect of these factors is that the melt process constitutes an attractive granulation technique, particularly whenever by-product or waste ammonium sulfate is priced solely on the basis of its contained ammonia.

SECTION VII

MARKET ANALYSIS

INTRODUCTION

A market analysis was made to determine national and regional consumption patterns of mixed fertilizer usage. Fertilizer ratios chosen for study in the project were selected for their ready acceptance by the farmer, as demonstrated in the results of market analysis.

ANALYSIS OF NATIONAL USE OF MIXED FERTILIZERS

The annual use of fertilizers for farm crop production in the United States has almost doubled over the period from the 1950's to the 1970's, increasing from about 22 million tons to 38 million tons. During the same years, the annual volume of mixed fertilizers increased from about 15 million tons to 22 million tons. Annual consumption is shown in Figure 8.

In these two decades, the average nutrient content of the fertilizer consumed in the United States also doubled[23], increasing from about 23 to 42%. These data are shown in Figure 9.

The combination of increase in volume of fertilizer used and in plant nutrient concentration of the fertilizer has increased farm nutrient consumption by a factor of four.

Figure 10 shows that the largest volumes of mixed fertilizers are used in three regions: the South Atlantic, the East North Central and the West North Central. In 1971, for example, these three regions (17 states) consumed 12.29 million metric tons (13.55 million short tons) of mixed fertilizer, or over half of the total volume consumed in the U.S. that year.

Table 18 shows grades of mixed fertilizers and the market share for each grade in 1970 and 1971. The columns are arranged in decreasing order with the highest demand grade of fertilizer listed at the top.

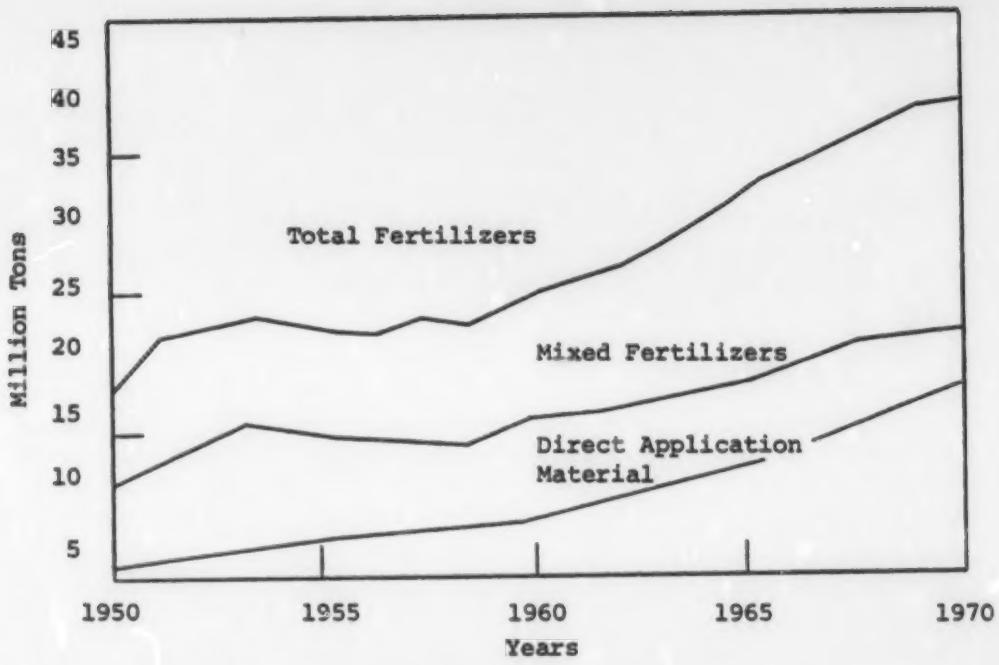


Figure 8. Fertilizer consumption in the U.S.

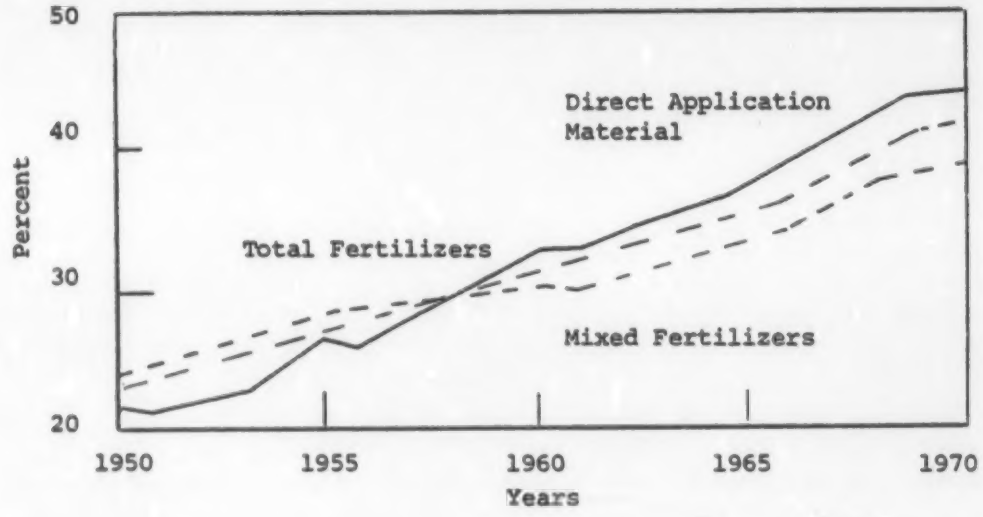


Figure 9. Average nutrient content of fertilizer.

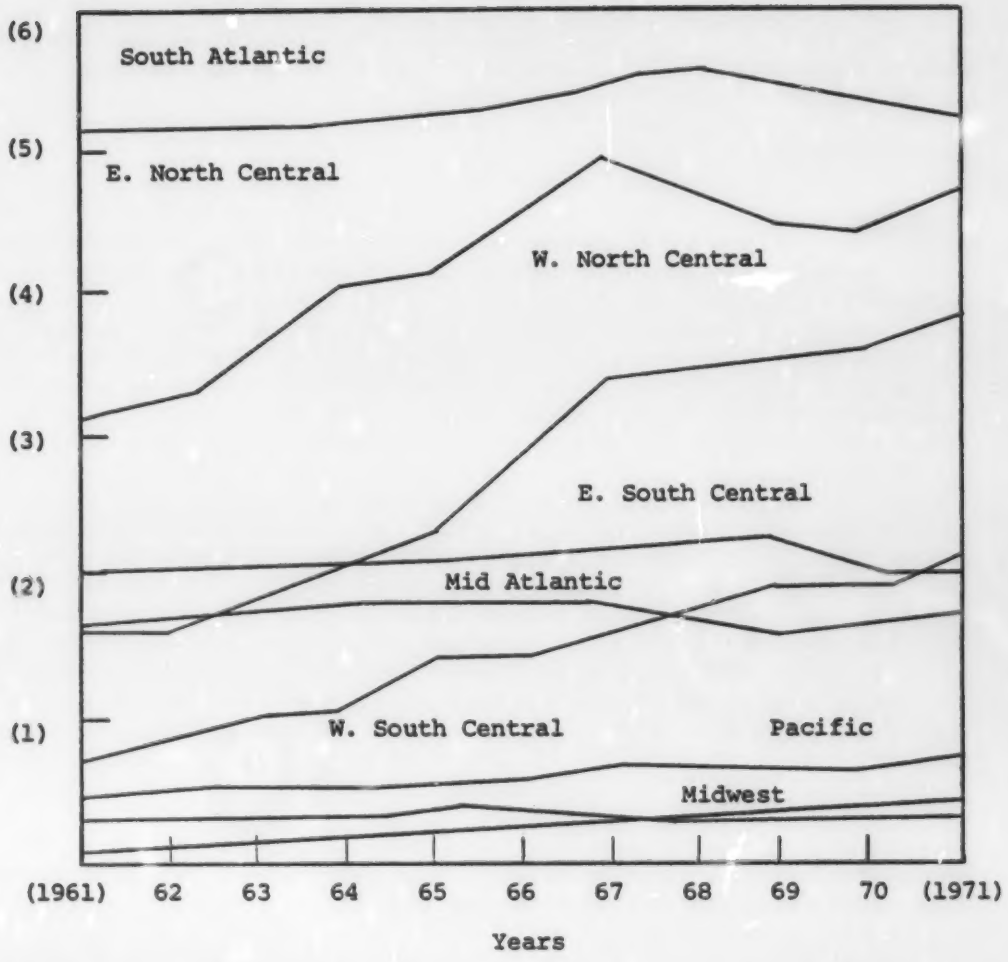


Figure 10. Consumption of mixed fertilizers.

The nutrient ratios of the fertilizers are also shown. Inspection of these data indicates that perhaps 25% of the mixed fertilizer grade ratios presently being used could offer a vehicle for the disposition of by-product or waste ammonium sulfate.

ANALYSIS OF REGIONAL USE OF MIXED FERTILIZERS

Table 19 shows the major grades of mixed fertilizer and the percent market share of each fertilizer in the significant agricultural regions in the U.S.A.

DEPLETION OF SULFUR IN SOILS

Sulfur is needed by plants and must be available in relatively large amounts for good crop growth. It is essential for synthesis of certain amino acids, for formation of chlorophyll and of some essential oils, and for formation or activation of several enzymes. In addition to satisfying these basic nutritional needs, sulfur sources may increase the availability of other essential nutrients and may be helpful in the reclamation of alkali and saline/alkali soils when applied to soils which are calcareous or which have high concentrations of hydrogen ions (high pH soils).[24]

Plants utilize sulfur in differing amounts according to species. For example, corn, sorghum and vegetables have relatively high sulfur requirements; legumes generally have intermediate requirements; most small grains and grasses need less sulfur. Crop sulfur requirements increase as higher yields are obtained. On soils which are both nitrogen and sulfur, or phosphorus and sulfur, deficient, and where the amounts of fertilizers being applied are on the order of the crop's normal requirements, fertilizer treatments of five to seven pounds of nitrogen for every pound of sulfur, or three pounds of P_2O_5 for every pound of sulfur, will be satisfactory for most cropping situations.[24]

Plants obtain their sulfur requirements from "soils, crop residues, and manure; from irrigation waters; from rainfall and atmosphere; and from fertilizers and soil amendments."[25]

Soils which are deficient in sulfur are found most often in humid regions of the country. Some humid soils contain large amounts of organic matter or hydrated oxides of aluminum or iron in which sulfates may have been absorbed. Such soils have relatively higher sulfur contents. In coarse-textured sandy soils, sulfates are lost readily by leaching. Most arid region soils contain large amounts of sulfate sulfur. However, such soils may provide poor water penetration or micro-nutrient availability. It may be possible to overcome such problems by the use of acid-forming sulfur materials.[25]

Table 18. CONSUMPTION OF FERTILIZER IN U.S. BY GRADE FOR 1970, 1971
(Percent of total)

Grade	1970	1971
18-46-0	7.31	8.03
6-24-20	5.81	5.94
5-10-15	4.39	3.86
10-10-16	4.00	3.79
5-10-10	3.70	3.27
12-12-12	3.02	2.86
8-32-16	2.17	2.18
10-20-20	1.98	2.17
10-20-10	2.85	2.00
13-13-15	1.69	1.90
6-12-12	2.41	1.84

Table 19. CONSUMPTION PERCENTAGES OF FERTILIZERS BY REGIONS AND GRADES, 1971

Region*	Grades and Percent of Total Mixed Fertilizer Use																			
% of Totals	18-48-0	16-16-16	15-15-15	13-13-13	12-12-12	10-34-0	10-20-20	10-20-10	10-15-15	10-10-10	8-32-16	8-24-24	6-24-24	6-12-12	5-10-15	5-10-10	4-12-15	3-9-18	3-9-9	0-20-20
North E. 48.8%[a]	1.9	–	11.9	–	2.1	–	1.8	2.3	16.1	8.1	–	–	–	–	–	4.6	–	–	–	–
N. Atlantic 45.1%	2.9	–	3.8	–	–	–	10.5	3.0	–	11.9	–	–	2.0	–	–	11.0	–	–	–	–
S. Atlantic 48.9%	–	–	–	–	–	–	2.2	–	–	7.7	–	–	–	2.0	12.6	8.6	4.0	5.0	6.8	–
E. N. Central 42.7%	8.7	2.1	1.1	–	5.7	1.6	–	–	–	–	5.3	–	18.2	–	–	–	–	–	–	–
W. N. Central 39.6%	20.5	–	–	–	3.7	3.3	–	–	–	–	5.1	–	7.0	–	–	–	–	–	–	–
E. S. Central 67.9%	1.7	2.4	2.2	12.4	–	–	2.0	–	–	6.4	–	8.2	2.8	12.3	6.6	–	6.5	–	–	4.4
W. S. Central 42.7%	8.9	–	–	3.8	6.0	1.6	1.8	14.4	–	–	–	1.5	3.1	–	–	–	–	–	–	1.6
Mountain St. 49.1%	42.2	–	–	–	–	6.9	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Pacific St. 16.3%	3.9	3.6	–	–	4.5	3.0	–	–	–	1.3	–	–	–	–	–	–	–	–	–	–

[a]Percent of total use accounted for U.S. 43.90%

Many soil areas in the United States are known or suspected to be sulfur deficient. Such areas occur in twenty states within the continental United States, as shown in Figure 11, as well as in Alaska and Hawaii. Almost all states contain areas which have a pH value exceeding 7. In these areas crop production would probably benefit from acidification in fertilizer bands or a more general downward adjustment of pH. Areas which contain coarse textured soils not presently considered sulfur deficient could readily become so. Such areas are shown in Figure 12.[26]

Crop residues and manure are sources of sulfur. However, the use of manure has decreased dramatically except near feedlot operations. Irrigation water which is derived from glaciers contains very small amounts of dissolved solids. Many inland water supplies are somewhat brackish, particularly in the Middle West and West, and may contain several hundred parts per million of sulfates. Sulfur emitted from the stacks of fossil-fuel burning power plants and industrial plants constitutes a potentially important sulfur source. However, most of this sulfur is deposited near the source of the emission rather than evenly throughout the country. Furthermore, as the requirements of the Clean Air Act become effective, less sulfur will be discharged into the atmosphere.[25]

The other major sources of sulfur are fertilizers and soil amendments. Until about 1950, normal superphosphate and ammonium sulfate were used in large quantities. These fertilizers contain 12 to 24% sulfur, respectively. When their use was supplanted by the introduction of concentrated fertilizers, which are less costly to transport and to apply to the soil, the use of sulfur-containing materials decreased sharply. As shown in Table 20, the total amount of sulfur contained in all applied fertilizers fell from 1.8 million tons in the 1949-50 crop year to 1.1 million tons in the 1972-73 crop year; at the same time the ratio of sulfur to the total of Nitrogen + Phosphorus Pentoxide + Potassium Oxide + Sulfur ($N + P_2O_5 + K_2O + S$) is estimated to have fallen from 0.31 in the 1949-50 crop year to 0.06 in the 1972-73 crop year.[25]

There is no generally recognized or accepted method for calculating the amount of sulfur that should be applied to crop lands. Two methods may be considered. These are:

1. Sulfur Replacement - An estimate is made of the total amount of sulfur removed by various crops. This is multiplied by a factor (estimated at 1.75 for sulfur) to correct for losses caused by leaching and for elements which limit efficiency of utilization for fertilizer applications.

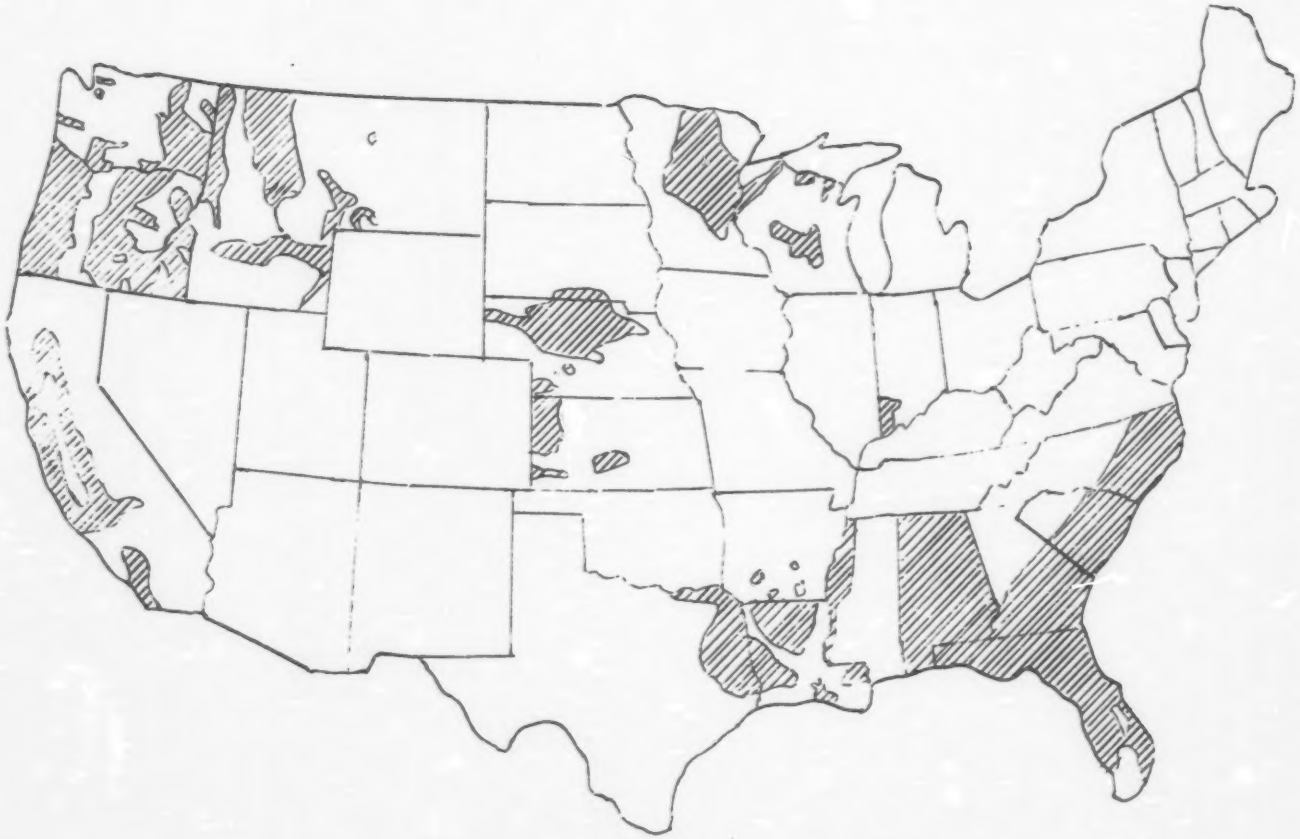


Figure 11. Soil areas in the U.S. known or suspected to be sulfur deficient.

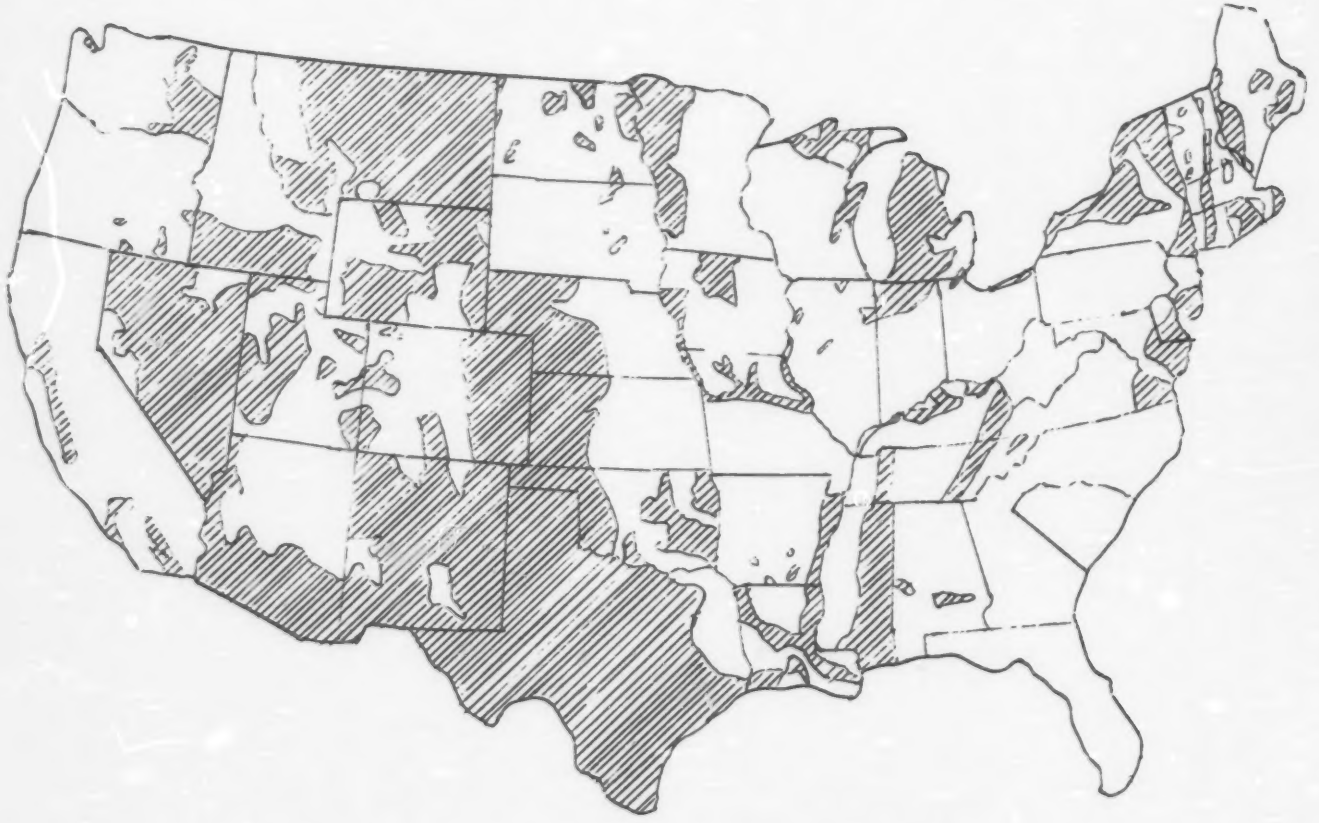


Figure 12. Soil areas in the U.S. where acidification probably would benefit crop production or which contain coarse textured soils which readily could become sulfur deficient.

Table 20. CONSUMPTION OF SULFUR-CONTAINING FERTILIZERS IN THE CONTINENTAL U.S.

Fertilizer Comsumption	Crop Year			
	1949/50	1959/50	1969/70	1972/73
	1000 Short Tons			
$N+P_2O_5+K_2O$	3,995	7,350	15,947	17,822
Total Contained Sulfur	1,803	1,486	1,272	1,088
Total Sulfur as Percent of $N+P_2O_5+K_2O+S$	31.3	16.8	7.4	5.8
Ratio of N:S in Fertilizers	0.5	1.8	5.8	7.6
Ratio of P_2O_5 in Fertilizers	1.1	1.7	3.6	4.6

2. Recommended application Rates - Recommended application rates may be projected for specific areas based on factors such as crop sulfur requirements, crop yields, soil conditions and application rates of other nutrients.

The results of estimates of sulfur requirements based on these two methods are shown in Table 21. Estimates of requirements based on sulfur replacement values were calculated from data on the three crop years of 1970-72. Estimates of requirements based on crop and soil conditions were calculated from data obtained prior to 1968. Table 21 also shows the total amount of sulfur in all fertilizer which was applied during the 1972-73 crop year.

The data presented in this table "indicate that the amount of sulfur added to crops in the United States in the form of fertilizer is insufficient to meet the requirements of the crops for this element. The balance of the crop's sulfur requirement is provided chiefly by soil sulfur reserves and by sulfur in the rain and atmosphere. Soil surface reserves are finite and exhaustible, and increasingly strict air pollution regulations are limiting the amount of sulfur oxides emitted to the atmosphere. Thus, the United State agriculture is operating on a negative sulfur balance."[25]

Table 21. SULFUR REQUIREMENTS AND FERTILIZER SULFUR APPLICATIONS
(Thousand short tons)

Estimated Sulfur Requirements By:	Cont'l U.S.	New England	Middle Atlantic	South Atlantic	E. North Central	E. South Central	W. North Central	W. South Central	Mountains	Pacific
1. Crop sulfur replacement (1970-72)										
Field crops	1298	14	67	84	313	55	471	177	86	91
Hay and pasture	2775	19	112	169	352	245	683	628	398	170
Total	4073	33	179	253	665	300	1154	745	484	261
2. Recommended application rates (prior to 1968)										
Field crops	1246	8	56	111	302	65	437	150	29	88
Hay and pasture	1248	15	54	98	87	68	313	195	86	49
Total	2494	23	110	209	389	133	750	345	115	420
Total Sulfur in Applied Fertilizers (1972-73)										
Field crops	927	7	49	148	164	49	167	90	74	179
Hay and pasture	160	3	9	35	14	30	20	34	9	7
Total	1087	10	58	183	178	79	187	124	83	186

SECTION VIII

REFERENCES

1. Lee, R. G., R. S. Meline, and R. D. Young. Pilot Plant Studies of an Anhydrous Melt Granulation Process for Ammonium Phosphate-Based Fertilizer. Proceedings of the International Superphosphate Manufacturers Association Technical Conference (Sandfjord, Norway). September 1970. Paper No. 5.

2. Kubasova, L. V., T. D. Pozlarskaya, and H. M. El Shinnawy. Potassium Polyphosphates. Vestnik Moskovskogo Universiteta, Khimiya. 11(6):680-685, 1970.

3. Moore, W. P. and W. C. Sierichs. Potassium Polyphosphates. U. S. Patent No. 3,607,018. Issued September 21, 1971.

4. Legal, C. C. Apparatus for Producing Ammonia Phosphate Fertilizers. U. S. Patent No. 3,482,945. Issued April 10, 1968.

5. Caricu, J. and O. Foubert. Ammonium Polyphosphates from Orthophosphoric Acid. French Patent No. 1,553,120. Issued January 10, 1969.

6. Carroll, R. L., J. H. Sims, B. L. Owens, and V. Reynolds, Jr. Ammonium Polyphosphates. German Patent No. 909,438. Issued November 13, 1969.

7. Farr, T. D. and H. K. Walters. Ammonium Polyphosphates Produced At Atmospheric Pressure. U. S. Patent No. 3,537,815. Issued November 3, 1970.

8. Kearns, T. C. Polyphosphate Fertilizers Made Via Simplified Route. Chemical Engineering. 76(27):94-96, 1969.

9. Hodge, C. A. Bench Scale Production of Ammonium Potassium Polyphosphates. Industrial and Engineering Chemistry, Product Research and Development. 10(4):437-441, 1971.

10. Knapsack, A. G. and G. M. B. H. Benckiser-Knapsack. Preparation of Ammonium Polyphosphates. French Patent No. 2,006,107. Issued December 19, 1969.

11. Vol'fkovich, S. I., L. V. Kubasova, O. R. Norchaeva, and L. S. Kulikova. Synthesis of Nitrogen-Phosphorus Fertilizer Based on the Intermediate Product of Urea and Phosphoric Acid Reaction. Zhurnal Prikladnoi Khmii. 42(5):979-984, 1969.

12. Vol'fkovich, S. I. and I. I. Checkovskikh. Urea Polyphosphates. U. S. S. R. Patent No. 296,743. Issued March 2, 1971.

13. Fleming, J. D. Polyphsophates Are Revolutionizing Fertilizers. Part I, What Polyphosphates Are. Farm Chemicals. 132(8):30-36, 1969.

14. Siegel, M. R. and R. D. Young. Polyphosphates Are Revolutionizing Fertilizers. Part II, Base Materials. Farm Chemicals. 132(9):41-47, 1969.

15. Achorn, F. P. and J. S. Lewis. Uses for Solid Ammonium Polyphosphates in Bulk Blending, Granulation and Fluid Fertilizers. Fertilizer Industry Round Table, Proceedings No. 18. 123-127.

16. Beglov, B. M., V. A. Budkov, and F. P. Chumakov. Physicochemical Properties of Granulated Fertilizer Mixtures Based on Ammonium Polyphosphates. Uzbekskii Khimicheskii Zhurnal. 15(2):76-78, 1971.

17. Achorn, F. P. and W. C. Scott. Polyphosphates Are Revolutionizing Fertilizers. Part III, Polyphosphates in Mixtures. Farm Chemicals. 132(12):46,48,50,51,192, 1969.

18. Slack, A. V., J. M. Potts, and H. B. Shaffer, Jr. Effect of Polyphosphates Content on Properties and Use of Liquid Fertilizers. Journal of Agricultural and Food Chemistry. 13(2):165-171, 1965.

19. Thiokol Chemical Corporation. Sulfur Encapsulates Fertilizer Pellets. British Patent No. 1,171,255. Issued November 19, 1969.

20. Fleming, P. S. Coating Fertilizers With Sulfur to Control Dissolution. U. S. Patent No. 3,576,613. Issued April 27, 1971.

21. Olson, R. A. (ed.). Fertilizer Technology and Use. Soil Science Society of America, Inc. Madison, Wisconsin. 1971.

22. U. S. Department of Agriculture. Commercial Fertilizers. Statistical Bulletin No. 472. Government Printing Office. Washington, D. C.

23. National Fertilizer Development Annual Reports, 1966-1974.

24. Bixby, D. W. and J. D. Beaton. Sulphur Containing Fertilizers. Technical Bulletin No. 17. The Sulphur Institute. Washington, D.C. December 1970.

25. Beaton, J. D., D. W. Bixby, S. L. Tisdale, and J. S. Platou. Fertilizer Sulphur. Technical Bulletin No. 21. The Sulphur Institute. Washington, D. C. August 1974.

26. Beaton, J. D., S. L. Tisdale, and J. Platou. Crop Responses to Sulphur in North America. Technical Bulletin No. 18. The Sulphur Institute. Washington, D. C. December 1971.

27. Esso Research and Engineering Company, Esso Research Agricultural Products Laboratory. Paper by Paul R. Geissler. Determination of the Critical Relative Humidity of Multi-Component Systems. 1966.

ADDITIONAL REFERENCES

Bauwens, R. and R. Julou. Preparation of Water-Soluble Ammonium Polyphosphates. German Patent No. 1,923,246. Issued November 20, 1969.

Bottai, G. A. and J. M. Stinson. Method For Urea-Ammonium Polyphosphate Production. U. S. Patent No. 3,578,433. Issued May 11, 1971.

Rohlfs, H. A. and H. Schmidt. Ammonium Polyphosphates. U. S. Patent No. 3,419,349. Issued December 31, 1968.

Siegel, M. R., R. S. Meline, and T. M. Kelso. High-Analysis Fertilizers From Phosphoric Acid and Conventional Ammoniating Materials. Journal of Agricultural and Food Chemistry. 10(5):350-361, 1962.

Vol'fkovich, S. I., A. I. Chekhovskikh, and T. K. Mikhaleva. Preparation of Urea Phosphates. Khimicheskaya Promyshlennost. 46(9):676-678, 1970.

Young, R. D., G. C. Hicks, and C. H. Davis. TVA Process for Production of Granular Diammonium Phosphate. Journal of Agricultural and Food Chemistry. 10(6):442-447, 1962.

SECTION IX

APPENDIX

LABORATORY INVESTIGATION

Table A-1 presents selected results of laboratory tests which were performed.

The following pages describe the procedures which were used to determine the moisture sensitivity of the product.

These data and techniques are discussed in Section IV.

Hygroscopicity Test 30° C (86° F)

Application - To determine the rate of water vapor absorption of product fertilizer granules.

Apparatus and Reagents -

Balance
Constant temperature chamber
Container to hold 15 grams (gms) of fertilizer in a monolayer. For example, a 100 x 15 millimeter (mm) Petri dish.

Concentrated sulfuric acid
40% (by weight) sulfuric acid
35% (by wt.) sulfuric acid
One to three dessicators

Procedure -

1. Condition approximately 15 gms of fertilizer for one week in a desiccator containing concentrated sulfuric acid at 30° C (86° F).

2. Weigh container and fertilizer accurately within 0.01 gm.

Table A-1. LABORATORY FORMULATIONS

Sample Number	Sample Symbol & Grade	Melt	Mix Formulation, Percent					Temperature, °C		Lab Analysis, Percent				Marketable Prod. -5/ +14 Mesh, %	Hardness, kg	Granulation Quality	Comments
			Melt	KCl	Recycle	AS	Fines	Solids	Reactor Melt	N	P_2O_5	PP	K_2O				
10-31-72	12-24-12	12-57-0	37.3	23.7	-	39.2	-	163	177	12.7	18.6	32	14.4	-	-	good	
11-02-72	14-14-14	48.6	24.7	22.1	-	53.2	-	163	246	13.5	16.4	42	14.0	31.2	5.0	good	
11-08-72	12-24-12	11.5-61-0	44.5	20.6	-	35.0	44.3	163	247	12.2	23.7	40	12.7	48.3	5.6	good	Mixed in two stages.
11-07-72	14-14-14	11.5-61-0	24.6	22.6	0.0	52.9	33.9	163	247	13.6	16.0	55	14.5	55.7	-	v. good	AS used; -40 mesh.
11-16-72	14-14-14	12-57-0	24.6	22.6	0.0	52.9	75.4	177	260	13.7	14.6	52	13.7	58.1	-	good	Mixed melt with aqua NH_3 heated to 260°C.
11-17-72	14-14-14	12-57-0	24.6	22.6	0.0	52.9	75.4	260	190	13.9	13.4	20	14.2	53.4	hard	good	Melt conditioned with aqua NH_3.
11-18-72	14-14-14	12-57-0	22.6	24.6	0.0	53.0	0.0	204	204	13.7	13.9	37	15.4	43.7	6.3	good	Granulation 30 seconds.
12-07-72	12-24-12	12-57-0	14.5	6.5	33.8	11.4	11.4	177	218	8.7	20.0	24	24.8	51.2	-	poor	Improper wetting of solids, pH 3.6.
12-12-72	14-14-14	12-52-0	46.8	43.0	0.0	10.1	53.1	163	204	13.6	16.1	41	13.0	59.1	-	good	
12-13-72	14-14-14	12-52-0	17.3	15.9	26.7	38.0	38.0	163	204	13.4	16.4	36	13.2	44.4	-	good	Very sticky hi poly content.
12-15-72	14-14-14	12-57-0	24.6	22.6	0.0	52.9	52.9	163	218	13.4	17.4	35	14.6	31.0	8.4	good	Attrition 19% (-14 mesh).
12-15-72	14-14-14	12-57-0	19.6	18.0	20.0	42.2	42.2	-	-	12.9	20.4	31	12.4	37.8	10.4		Low attrition, pH 2.7.
12-21-72	14-24-08	12-57-0	32.0	9.8	25.4	32.7	42.6	121	190	12.9	28.4	22	7.4	62.7	-	v. good	Solids and melt mixed till crystallization started, then granulation started.
										(With tee reactor)							
02-22-72	14-14-14	Lab. Re.	24.6	22.5	0.0	52.9	0.0	190	219	14.0	20.8	20	9.9	61.2	-	v. good	Reactor 219°C, pH high.
02-24-72	14-14-14	Lab. Re.	24.9	23.2	0.0	49.6	49.6	204	204	13.2	12.8	36	17.1	41.0	-	-	Urea crystal 2%, pH 4.5, too hot; by crushing hot some granulation occurred.
02-24-72	14-14-14	Lab. Re.	24.5	22.5	0.0	52.9	52.9	200	204	14.2	20.0	21	8.7	51.9	5.0	v. good	Initial pH 4.7, lab analysis.
02-27-72	14-14-14	Lab. Re.	24.6	22.5	0.0	52.9	0.0	200	216	13.6	14.5	23	14.5	50.5	-	good	pH 4.2, KCl +20 mesh.
03-05-72	14-14-14	Lab. Re.	24.6	22.6	-	52.9	26.5	200	210	14.1	14.2	26	13.0	41.5	-	good	pH 4.8, KCl not completely wetted.
03-05-72	14-14-14	Lab. Re.	24.6	22.6	-	52.9	13.2	200	216	14.2	14.3	29	13.6	68.7	-	good	pH 4.4, too much melt or solids too hot.
03-4-72	14-14-14	Lab. Re.	24.6	22.6	-	52.9	none	200	247	-	-	59	59.0	-	81.0	good	Concentrated acid, sticky product cooled slowly.
03-19-72	14-14-14	Lab. Re.	24.6	22.6	-	52.9	13.2	-	-	14.1	15.1	39	14.16	-	-	-	pH 3.5.

3. Place weighed container with fertilizer in a desiccator containing 40% sulfuric acid in a 30° C (86° F) constant temperature chamber.

4. Weigh container each day for five to seven days to establish moisture pick-up rate.

5. Repeat test using 35% sulfuric acid.

Calculations -

(Wt. after being in chamber - initial dry wt.) X 100/initial dry wt. = % moisture absorbed.

Rate of Solution Test for Granular Fertilizers

Application - To determine the solubility rate of fertilizers at controlled conditions.

Apparatus and Reagents -

Long stem glass funnel
100 milliliter (ml) graduated cylinder
Thermometer
Constant temperature bath

Procedure -

1. Select 50 gms of fertilizer passing through a 5 mesh but retained on a 14 mesh screen (U.S. Standard).

2. Place the fertilizer in the funnel; pour through 100 ml of distilled water at 10° C (50° F).

3. Recirculate this 100 ml of water at two-minute intervals for ten minutes for a total of six passes.

4. Analyze liquid for N, P, K and pH.*

*pH measurement used to make approximation of mole ratio NH_3/P_2O_5

Calculations -

Present data as %N, %P_2O_5, %K in liquid.

Rate of Hydrolysis Test

Application - To determine the reversion rate of polyphosphates to the ortho form.

Apparatus and Reagents -

25% (by wt.) sulfuric acid solution
Four containers that hold approximately 15 gm of fertilizer in a monolayer
One or more desiccators
One constant temperature chamber

Procedure -

1. Place approximately 15 gms of fertilizer in three different containers in the desiccator after recording the total weight of each container of fertilizer.
2. Place desiccator in chamber at 30° C (86° F).
3. After one week, remove one container and analyze for N, total P_2O_5, non-ortho P_2O_5, K and water content,
4. Repeat Step 3 after two and three weeks.

Hygroscopicity of Complex Fertilizers

Application - A vacuum line technique is described for the measurement of the equilibrium relative humidity of complex fertilizers. It consists of determining the vapor pressure of the saturated solution that is formed on the surface of such fertilizers by the absorption of small amounts of water vapor. Application of this method to systems of binary mixtures, reciprocal salt pairs and commercial fertilizers containing several components is discussed. The main advantage of this method is that it can measure critical relative humidities of samples over a wide range of measurable water concentrations even at the low concentrations usually found under storage conditions.[27]

Procedure - The pertinent parts of the glass vacuum line used in this method are shown schematically in Figure A-1. The line consists of a water reservoir and thermostat sample containers that can be filled with water vapor, isolated by means of a stopcock from the rest of the vacuum line, and mamometers to measure the vapor pressure inside the sample containers. The vacuum line is wrapped with nicrome heating wire to prevent the condensation of water vapor on cold spots.

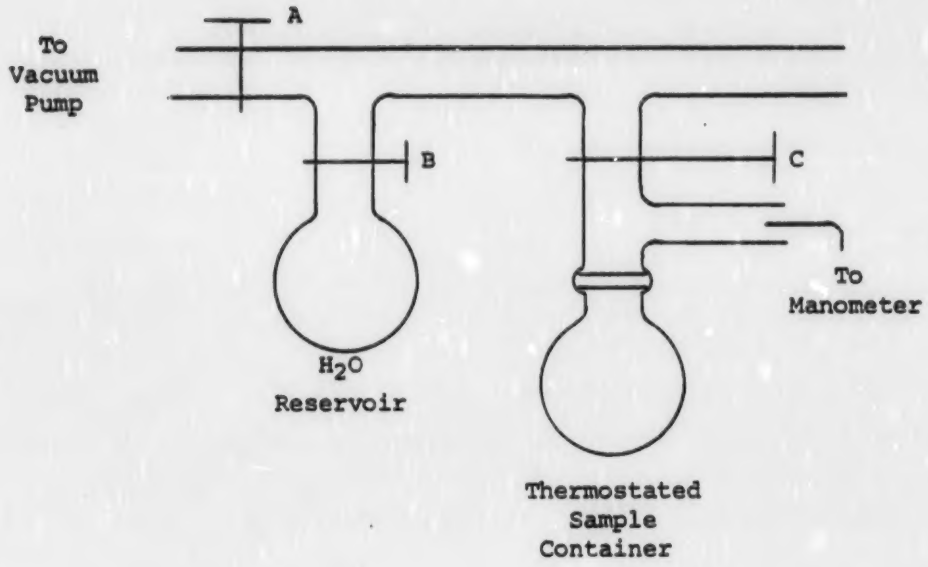


Figure A-1. Vacuum line for measuring critical relative humidities of fertilizers.

The critical relative humidity of a fertilizer is determined by placing a 1 to 5 gm sample in a 25 ml round bottom flask which is attached to the vacuum line by means of a greased standard tapered joint, Figure A-1. The sample is then allowed to come to thermal equilibrium at the desired temperature. With Stopcocks A and C open and B closed, the system is evacuated to a pressure of less than 0.001 mm of mercury. Stopcock A is then closed and B opened, filling the sample containers with water vapor. The temperature of the water reservoir must be at least as high as that of the thermostated sample to ensure that water vapor fills the sample containers to pressures greater than the vapor pressure of the saturated solution. The water in the reservoir must be previously degassed so that the pressure of water vapor alone is being measured in the sample containers. Stopcock C is closed at any time after B is opened, and the decrease in vapor pressure is recorded as a function of time as the sample absorbs water. The pressure at equilibrium is taken to be the vapor pressure of the saturated solution of the sample, and its critical relative humidity is equal to that pressure divided by the vapor pressure of pure water at the temperature of the sample.

The amount of water absorbed can be varied by changing the time interval during which the sample is exposed to the water reservoir. By weighing the sample before and after a determination and knowing the absolute water concentration of the original sample, the amount of water absorbed can be measured. Thus, the critical relative humidity of a fertilizer can easily be studied as a function of % water over a wide range of water concentrations.

Equilibrium can also be approached by the absorption of water vapor from wet fertilizers. This is done by allowing the fertilizer sample to absorb water as above. Stopcock B is then closed and, with C open, Stopcock A is opened for a short time so as to evacuate the water vapor from the sample container. The sample is then isolated by closing Stopcock C. The increase of vapor pressure as water evaporates from the wet surface is recorded as a function of time until equilibrium is reached.

The two methods of approach to equilibrium have been found to give identical results in all of the systems investigated, although the attainment of equilbrium by absorption of water vapor is the method used in the majority of the cases studied. At a given temperature, the rate at which equilibrium is approached depends on many factors, such as surface area, particle size and water content of the sample. In actual practice, using 5 gm samples ground to pass through 80 mesh, equilibrium is reached at room temperature in less than one hour when the amount of water absorbed is about 1% of the total sample weight. Use of unground samples does not change the equilibrium values obtained, but does require longer time.

PILOT PLANT INVESTIGATIONS

Alternate I Design

Figure A-2 presents a flow sheet and material balance for a plant utilizing the Alternate I design referred to in Section V. It is included only in the Appendix because the cost analyses of Section VI showed that Alternate I is not as economical as Alternates II and III. No pilot plant work was done on this design.

The Alternate I design contains the following steps:

1. Melt production - The method of producing the ammonium polyphosphate melt is similar to that of Alternate II.

2. Mixing the melt with solid material - A preheated mix of dry materials, ammonium sulfate, potassium chloride, filler and recycle is introduced and mixed with the melt.

3. Sizing, recycle and storage - The mixed product is used to exchange heat with the raw feed. It is sieved for recycle, crushed and marketed or stored.

Thus, it may be seen that the Alternate I design embodies the same process concepts as Alternates II and III, which are reviewed in detail in Section V, but with the following key differences:

1. In Alternates II and III, a series of preheaters and partial coolers is added to more efficiently utilize heat which normally would be wasted.

2. In Alternate I, all mixing of dry product with raw materials occurs prior to the single point injection into the pug mill.

3. In Alternate I, no means are provided for sparging ammonia into the pug mill.

Alternates II and III Design

Table A-2 presents a summary of the calculations of the energy balances for the production of 13-13-13-13 and 12-24-12-13 grade fertilizers in the 454 kg/hr pilot plant using the melt process. This energy balance is applicable to both design alternates.

STREAM Nº	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩	⑪	⑫	⑬	⑭	⑮	⑯	⑰	⑱
DESCRIPTION	H_3PO_4	NH_3	H_2O VAP	STM	REC-YCLE	AS	KCL	FILL	MIX	MELT	PROD	+5	PROD	PROD	-14	PROD	REC-YCLE	MIX
FLOW (TPH) METRIC	11.2	1.45	3.18	3.36	41.3	22	9.5	—	72.8	9.9	82.5	8.2	41.3	22.2	19	41.3	41.3	90.7
TEMP °C	21	21	149	265	115	21	21	—	132	265	171	115	115	115	115	71	115	115

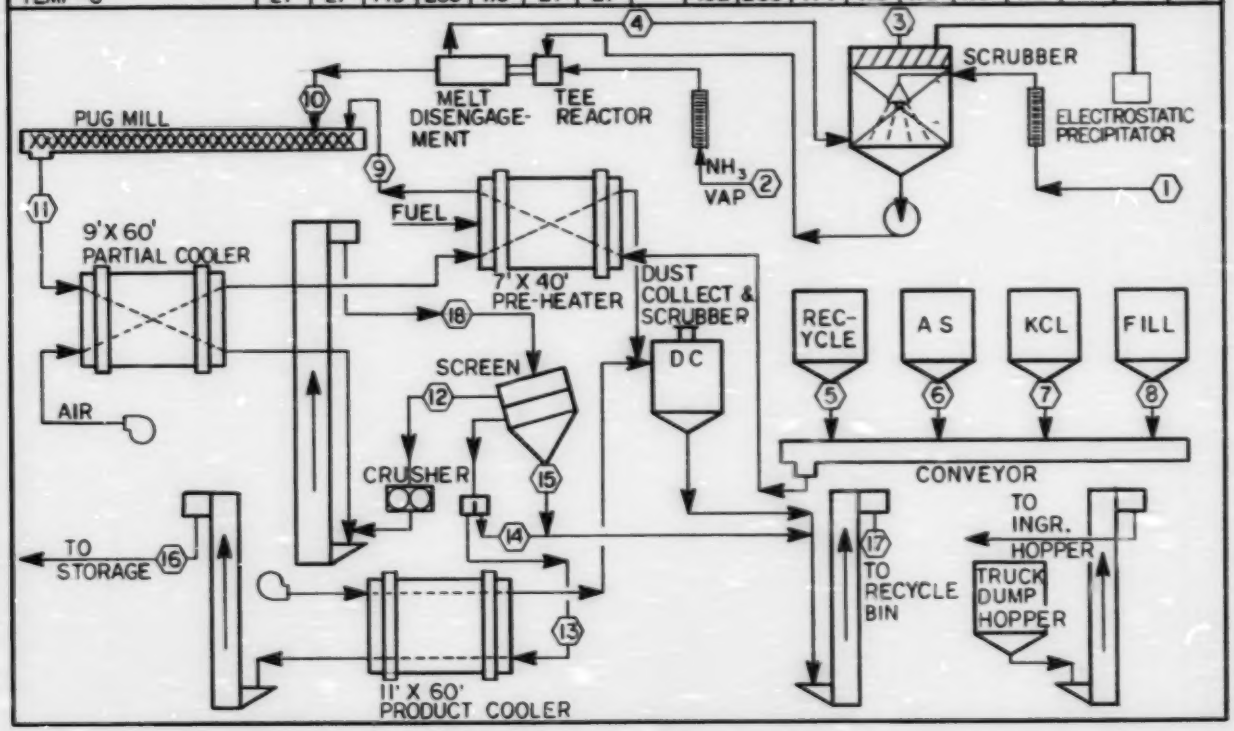


Figure A-2. Alternate I flow sheet for 907 Mt/d (1000 st/d) pilot plant producing grade 13-13-13-13.

Table A-2. ENERGY BALANCE CALCULATIONS FOR 454 kg/hr (1000 lb/hr) PILOT PLANT

FOR 13-13-13-13 GRADE PRODUCT

Ingredients	Kg/t of product	(Lb/t of product)
Phosphoric acid 56%	232 (wet) 197 (dry)	(463) (wet) (395) (dry)
Ammonia, anhydrous	35	(70)
Ammonium sulfate	485	(970)
Potassium chloride (61.5% K)	212	(423)

From the reactor:

NH_3 (gas) + H_3PO_4 (liquid) $\rightleftharpoons$ $NH_3H_2PO_4$ (crystalline)

H_f -11.04 -305.6 -345.28 kcal/g-mole

(21°C) H_R = 28.64* kcal released/g-mole

*Heat absorbed in polyphosphate formation included (2900 BTU/t equivalent).

Heat released based upon NH_3:

28.64 kcal/g-mole/17 gm/g-mole = 1.85 kcal/g, or 1685 kcal/kg NH_3
28.64 (kcal/g-mole)/17 g-mole x 1800 (conversion factor)
= 3032 BTU/lb NH_3

The heat released (total heat generated):

35 kg NH_3/t product x 1685 kcal/kg NH_3 = 58,975 kcal/t product
(70 lb NH_3/t product x 3032 BTU/lb NH_3 = 212,240 BTU/t product)

Assume a melt temperature in the tee reactor of 121°C (250°F). If ambient acid and ammonia gas feed temperature is 21°C (70°F), then the sensible heat required becomes:

232 kg acid/t product x (121° - 21°C) x 0.53 (specific heat)
= 12,296 kcal/t product.

(463 lb acid/t product x [250° - 70°F] x 0.53 specific heat
= 44,170 BTU/t product).

Table A-2 (continued). ENERGY BALANCE CALCULATIONS FOR 454 kg/hr (1000 lb/hr) PILOT PLANT

30 kg NH_3/t product x (121° - 21°C) x 1.1 (specific heat)
= 3,850 kcal/t product.

(70 lb NH_3/t product x [250° - 70°F] x 1.1 [specific heat]
= 13,860 BTU/t product).

Total sensible heat = 16,146 kcal/t product
(58,030 BTU/t product)

Evaporation of water at 100°C (212°F) assumes 540 kcal/km (970 BTU/lb).
35 kg H_2O/t product x 540 kcal/kg = 18,900 kcal/t product
(68 lb H_2O/t product x 970 BTU/lb = 65,960 BTU/t product)

Solid ingredients:* (Assume heated to 130°C by reactor heat)

707 kg/t product (130° - 21°C) x 0.26 (specific heat)
= 19,753 kcal/t product.

(1393 lb/t product [266° - 70°F] x 0.26 [specific heat]
= 70,987 BTU/t product).

*Alternate I - Sensible heat of solid ingredients is furnished by an external heat source. This added heat must then be removed during cooling.

Heat utilized:

	kcal/t	(BTU/t)
Sensible heat	16,146	(58,030)
Water (latent heat)	18,800	(65,960)
Solids	19,753	(70,987)
Total	54,799	(194,977)

Heat remaining in product:

	kcal/t	(BTU/t)
Total heat generated	68,975	(212,240)
Heat consumed	54,799	(194,977)
Heat remaining	4,176	(17,263)

Estimated ambient heat losses: 4,176.

Table A-2 (continued). ENERGY BALANCE CALCULATIONS FOR 454 kg/hr (1000 lb/hr) PILOT PLANT

FOR 12-24-12-13 GRADE PRODUCT

Ingredients	Kg/t of product	(Lb/t of product)
Phosphoric acid 54%	428 (wet)	(855) (wet)
	365 (dry)	(730) (dry)
Ammonia, anhydrous	60	(120)
Ammonium sulfate	336	(672)
Potassium chloride (61.5%)	196	(392)

Heat released by chemical reaction:

101,100 kcal/t product
(363,840 BTU/t product)

Melt temperature in the tee reactor: 121°C (250°F)
Ambient temperature: 21°C (70°F)

Heat consumed:

	kcal/t	(BTU/t)
Sensible heat	29,284	105,327
H_2O	34,020	121,250
Solids	15,354	74,693
Total	78,658	301,270

Heat remaining in product:

	kcal/t	(BTU/t)
Total heat generated	101,100	(363,840)
Heat consumed	78,658	(301,270)
Heat remaining	22,442	(62,570)
Estimated ambient heat losses:	10,760	(30,000)

Alternates II and III Pilot Plant Test Data

Table A-3 presents selected results of the 45 kg/hr pilot plant tests. This data is discussed in Section V.

Table A-3. PILOT PLANT OPERATION IN 45 kg/hr (100 lb/hr) PLANT

Sample	Analysis, %				pH	Marketable Product -5/+14 mesh, %	Reactor Temp., °C	Comments
	N	P_2O_5	Poly P	K_2O				
5/29	12.72	23.43	29.4	10.22	3.7	-	218	Heated acid, heated solid to 149° C, crystallization of melt on pug mill.
6/15	9.46	16.10	17.3	23.64	3.4	-	-	Heated acid, sensitive to liquid and over-agglomeration followed by under-agglomeration.
6/25	2.80	9.37	29.7	47.09	6.0	-	218	Add KCl and ammonium sulfate in pug mill to force crystallization recycle minimum.
6/28	2.77	9.66	28.8	48.09	5.6	-	228	54% phosphoric acid.
7/11	11.91	17.93	56.7	19.8	4.6	-	225	Raw materials added at center, recycle sulfate, ammoniation in tee reactor and pug mill.
7/14	11.56	13.00	28.1	20.8	5.4	83.9	218	Fine ammonium sulfate, ammoniation tee reactor, pug mill, 9% attrition.
7/16	13.56	13.89	29.0	15.3	5.4	82.8	218-232	Ammoniated in tee reactor and pug mill, good granulation, low attrition.
7/18	12.94	17.48	37.6	14.83	5.1	-	-	Ammoniation in pug mill and tee reactor, recycle temperature 107° C, very uniform granulation, 1 lb/hr ammonium in pug mill.
7/19a	12.27	22.11	25.7	15.03	4.8	82.2	-	Recycle 107° C, melt added upstream, ammoniation in pug mill.
7/19b	12.35	20.92	30.0	14.03	4.7	98.8	-	Recycle 107° C, ammoniation in pug mill increased the liquid phase, 8.4% attrition.
7/25	14.20	18.37	36.6	11.22	4.4	-	238	Heated solids, excess fluidity in pug mill.
7/27	14.84	19.22	28.5	8.21	4.7	91.7	238	Heated recycle, recycle balanced 3% attrition.
7/27	14.84	19.22	28.5	8.21	4.7	91.7	238	Heated recycle, recycle balanced, 3% attrition.
7/30	14.93	13.90	33.0	10.82	5.4	90.2	232	Heated recycle, 4% attrition.
7/31	13.92	15.33	25.7	14.02	5.4	88.2	238	Reactor temperature of 204° C caused tee reactor to start plugging 7.3% attrition.
8/09	13.58	14.34	40.6	15.13	4.7	-	275	Heated acid and recycle to 149° C, granules had a "wet" appearance, large particles produced, granules very tacky.
9/06	14.97	11.24	30.3	11.42	5.1	-	246	Recycled all recycle material.
9/11	15.52	11.95	31.3	9.92	5.1	-	-	Heated recycle, good mixing, solids took on cohesive appearance prior to melt addition.
9/14a	14.17	19.37	36.6	11.70	4.7	-	222	Heated recycle, problem of buildup in pug mill.
9/14b	14.54	15.23	31.1	11.9	4.9	-	223	Heated recycle, clean section of shaft in pug mill assisted operation.